Volume 55 December 1960 Number 8

Economic Geology

and the

Bulletin of the Society of Economic Geologists

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PUBLISHED SEMI-QUARTERLY

Eight Dollars Fifty Cents a Year, One Dollar Fifty Cents a Copy

THE ECONOMIC GEOLOGY PUBLISHING COMPANY

Printed by Lancaster Press, Inc., Prince and Lemon Streets, Lancaster, Pa.

Second-class postage paid at Lancaster, Pa.

Economic Geology

and the

Bulletin of the Society of Economic Geologists

Issued Semi-Quarterly (Jan.-Feb., Mar.-Apr., May, June-July, Aug., Sept.-Oct., Nov. and Dec.) and sent to subscribers on or about the following dates: February 1, March 15, May 1, June 15, August 1, September 15, November 1, December 15.

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Indexed in the Industrial Art Series.

LANCASTER PRESS, INC., LANCASTER, PA.

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VOL. 55 DECEMBER, 1960 NO. 8

SULFUR ISOTOPE INVESTIGATION OF THE GOLD-QUARTZ DEPOSITS OF THE YELLOWKNIFE DISTRICT[1]

R. K. WANLESS, R. W. BOYLE, AND J. A. LOWDON

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ABSTRACT

Sulfides in the orebodies and their associated alteration haloes, the metamorphic facies of the greenstone belt, and the neighboring granodiorite have been examined in detail. Most of the samples investigated are slightly enriched in S^{34} with respect to the meteoritic standard. Although the overall range is small (about 1.5%), significant variations were found between sulfides in the granodiorite and in the metamorphic facies of the greenstone belt. A direct correlation exists between the isotopic ratio and the distance from the granodiorite-greenstone contact; sulfides in the granodiorite are the most enriched in S^{34} whereas sulfides in the metamorphic facies contain progressively less S^{34} outward from the granodiorite contact.

Sulfides in early tension fractures are consistently lighter (i.e. they contain more S^{32}) than the sulfides in the surrounding greenstones, whereas sulfides in the later gold-quartz lenses are heavier than those in the associated alteration zones. In addition, profiles across the country rock, alteration zones, and gold-quartz lenses indicate that the heavy isotope has been preferentially retained in the alteration zones with the maximum enrichment in the ore. However, in the late cross-cutting quartz-carbonate lenses the lighter sulfur isotope has been preferentially concentrated.

The isotopic studies indicate that the primary sulfur isotopic distribution of the district was modified by granitization and metamorphism during which the S^{32} was mobilized to a greater extent, leaving the sulfides in the regions with the higher thermal histories enriched in S^{34}. The subsequent formation of the gold-quartz lenses was associated with intense chemical activity and the S^{32} was again more mobile, resulting in an enrichment of S^{34} in the alteration zones and in the ore.

INTRODUCTION

For several years the Geological Survey of Canada has carried out a detailed geological and geochemical investigation of the gold-quartz deposits of the Yellowknife District, Northwest Territories, the results of which may be found in publications noted in the references. Recently, facilities for isotope research have been developed in the Survey laboratories in Ottawa, and a sulfur isotope investigation of the region undertaken.

One interpretation of the geochemical data obtained, suggests that the ore constituents of the gold-quartz orebodies were derived from the associated country rocks by diffusion. If this is the case, and the process of metamorphic secretion was responsible for the formation of the orebodies, the possibility exists that the isotopes of sulfur may have been fractionated, and the observed isotopic ratios may be indicative of the mechanism responsible for the concentration of the ore. This investigation has revealed that although the overall isotopic variation is small, significant trends are distinguishable. The majority of the specimens examined contain sulfur enriched in the heavier isotope (i.e. S^{34}) compared with the meteoritic troilite sample employed as a standard.

The sulfur isotope distribution has been correlated with the geology and geochemistry of the district and evidence is presented to support the hypothesis that the lighter sulfur isotope (i.e. S^{32}) has been mobilized more readily and that the residual sulfur has been consequently enriched in the heavier isotope. The observed enrichment is attributed to two distinct processes believed to be subsequent in time. These are: 1) a thermal gradient produced during early granitization and regional metamorphism, and 2) chemical and pressure gradients developed during the subsequent formation of the large shear zones containing the gold-quartz orebodies.

GEOLOGICAL SETTING OF THE DEPOSITS

The general geology of the Yellowknife district was described first by Stockwell and Kidd (22) and later, in more detail, by Jolliffe (14, 15). More recently a description of the geology and a structural analysis of the principal ore-bearing shear zones of the greenstone belt was published by Henderson and Brown (13). The geology of the orebodies of the Con-Rycon and Giant Mines was described by Campbell (8), Dadson and Bateman (12), Dadson (11), Bateman (2), Brown and Dadson (6), Boyle (5), and Brown, Dadson and Wrigglesworth (7). The mineralogy of the orebodies has been described by Ridland (20) and Coleman (9, 10). These authors have covered the geology and mineralogy of the district and gold deposits in considerable detail, and the brief description that follows gives a summary of the most important features and provides a background for discussing the isotope geology of sulfur within the district.

The consolidated rocks within the district are Precambrian in age (4, Fig. 1, p. 1508). The oldest rocks are greenstones consisting of a succession of massive and pillowed andesite and basalt flows with interbedded dacite flows, graphitic and siliceous tuffs, and agglomerates (Division A, Yellowknife Group). These rocks contain numerous gabbro and diorite sills and are cut by dikes of similar composition. Quartz-feldspar porphyry dikes and masses cut the greenstones throughout the district, but are found in greatest profusion in the northern part of the belt, particularly in the area east and southeast of Ryan Lake. The greenstones are overlain by a thick series of greywacke, argillite, slate, quartzite, and their metamorphic equivalents (Division B, Yellowknife Group).

Three large granitic masses occur within the district. One flanks the greenstone belt on the west, and another forms a large mass south of the sedimentary area. The third granitic mass, known as the Prosperous Lake granite, occurs east of Prosperous Lake. Field and chemical evidence suggest that the western granitic mass originated by granitization of a great series of sedimentary rocks that once lay stratigraphically below the greenstones. The Prosperous Lake granite and southeastern granitic mass were probably derived by granitization of parts of the Yellowknife sediments.

The greenstones have been extensively altered by regional metamorphism. The metamorphic facies (4, Fig. 2, p. 1509) are distinctly related to the granodiorite-greenstone contact and comprise a contact amphibolite facies, an

intermediate epidote amphibolite facies, and a poorly developed greenschist facies

Two metamorphic facies are clearly defined in the Yellowknife sediments and are related to the Prosperous Lake and southeastern granitic masses (4). Next to these granitic masses a zone of nodular quartz-mica schist and hornfels containing garnet, andalusite, staurolite, and cordierite is present. This facies grades sharply into relatively unaltered greywacke, argillite, arkose, and slate.

Pegmatites, containing quartz, feldspar, mica, and locally typical pegmatite minerals such as tourmaline, beryl, and spodumene, are abundant in the Prosperous Lake granite and the quartz-mica schist and hornfels facies of the Yellowknife sediments.

Diabase dikes and basic sills are the youngest consolidated rocks in the district. These have a gabbroic to ultra-basic composition and are relatively unaltered except where cut by late faults.

The greenstone rocks of the district are folded into a broad northeasterly-plunging asymmetrical syncline. The northwest limb (greenstone belt) consists of a simple homoclinal succession of volcanic flows that dip and face southeast. The southeast limb is overturned and is in part folded into a subsidiary anticline. The sediments of the Yellowknife group are complexly folded into tight isoclinal folds, which in turn have been cross-folded.

Two ages of shear zones occur in the greenstone belt (4): (a) early shear zones that parallel the lava flows in strike and dip and contain a few small high grade gold-quartz lenses, e.g. Ranney system; and, (b) shear zones that transect the lava flows and contain the large economic gold-quartz veins and lenses of the district, e.g. Con system. The Giant-Campbell shear zone system is the major ore-bearing system in the district and probably formed along a major thrust fault zone. The smaller but productive Con and Negus-Rycon systems are subsidiaries of this large system.

In the shear zone systems the principal ore controls are shear zone junctions and flexures and drag-folded parts of the large schist zones. The deposits are veins, lenses, and complex bodies of quartz enveloped by distinctive alteration haloes (Fig. 1).

In the sediments of the Yellowknife group, gold-quartz veins and lenses are developed in small faults, drag folds, saddle reefs, ruptured and sheared axes of isoclinal folds, and other structures, all formed during the complex folding of the sedimentary rocks. Structurally these veins and lenses are isolated bodies, unconnected to any system of fractures or faults along which hydrothermal solutions could have travelled.

Some of the gold-quartz lenses in the greenstones cut the last phase of granite dikes; therefore, it can be assumed that the deposits were formed after the emplacement and consolidation of the granitic mass flanking the greenstone belt. The lenses also cut the quartz-feldspar porphyry dikes and masses, thus ruling out the possibility that these bodies were the source of hydrothermal solutions from which the lenses were derived. In the sedimentary area the quartz lenses and veins appear to be contemporaneous with

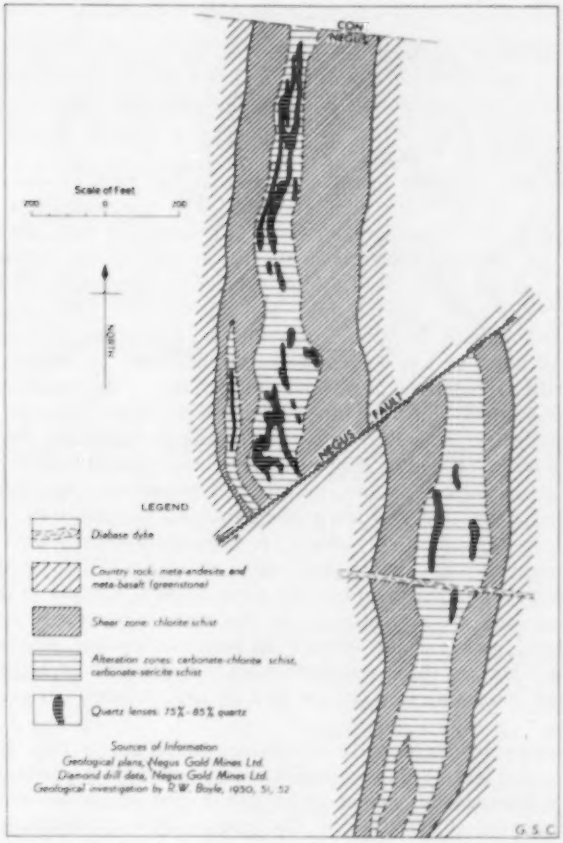

FIG. 1. Plan of geology, 1,775-foot level, Negus Mine, Campbell System.

the metamorphism of the sediments and the formation of the Prosperous Lake granite.

Post-diabase faults and fractures cut all rocks in the district. In these faults quartz-hematite lenses and "giant quartz veins" are localized at or near junctions and flexures.

MINERALIZATION OF THE DISTRICT

The age relationships of the various quartz, carbonate, and sulfide deposits are listed below, the oldest first. Pertinent features of each type of deposit are included.

Greenstone Belt

1. Formation of quartz lenses in tension fractures in massive flows and dikes. These lenses contain essentially quartz with minor amounts of pyrite. They exhibit no marked alteration zones, but chemical analyses on traverses across the rocks adjacent to the lenses suggest a transfer of silica from the walls into the tension fractures (5).

2. Formation of quartz lenses and veins in (a) parallel shear zone systems; (b) transecting shear zone systems. The age relationships of these two types of quartz lenses are uncertain. Presumably they are contemporaneous. The principal minerals in the lenses are quartz, carbonates, sericite, pyrite, arsenopyrite, chalcopyrite, sphalerite, pyrrhotite, scheelite, stibnite, various sulfosalts, galena, gold, and aurostibite. The paragenetic sequence of the sulfides is pyrite, arsenopyrite, pyrrhotite, chalcopyrite, and sphalerite, all more or less contemporaneous, followed by stibnite, sulfosalts, galena, locally sphalerite, gold, and aurostibite. The quartz lenses are generally enveloped by a carbonate-sericite-pyrite-arsenopyrite alteration halo that grades imperceptibly into the chlorite-carbonate or chlorite schist of the shear zones (Fig. 1). Chemical analyses of the alteration zones indicate that carbon dioxide, water, sulfur, and potassium were added to the highly altered zones, and that some silica, calcium, sodium, iron, magnesium, and manganese were removed. Boyle (3, 4, 5) has presented data suggesting that the carbon dioxide, water, and sulfur were derived from the country rocks and that they were drawn into the shear zones as a result of the pressure gradients resulting from dilatancy. In the shear zones these volatile compounds reacted with various silicates to form carbonates, sericite, chlorite, and sulfides. During these reactions silica was released in large quantities and migrated into, and was precipitated in local dilatant zones within the shear zones.

3. Formation of quartz-carbonate stringers and lenses that cross-cut the early gold-quartz lenses. These bodies contain essentially quartz, carbonates, chalcopyrite, tetrahedrite, galena, arsenopyrite, and minor amounts of sulfosalts; alteration haloes are absent. The quartz-carbonate stringers and lenses are isolated bodies and appear to represent fillings of tension fractures. The available facts suggest that their constituent elements were derived locally from the shear zones and early gold-quartz lenses.

4. Formation of late faults and fractures followed by deposition of quartz lenses and "giant quartz veins." These bodies contain essentially quartz and hematite with small quantities of pyrite and chalcopyrite. The principal alteration effects in the rocks adjacent to the quartz bodies are a mild silicification, sericitization, and chloritization.

5. Precipitation of carbonates and pyrite from underground waters carrying various sulfates, chlorides, and carbonates. This late mineralization is presently active.

Sedimentary Area

1. Formation of pegmatites containing essentially feldspar, quartz, muscovite, tourmaline, and locally beryl, spodumene, and tantalite-columbite.

Sulfides are rare or absent. The age of the pegmatites with respect to the quartz bodies described below is uncertain. Some pegmatites are cut by these quartz bodies; others cut across the gold-quartz lenses.

2. Formation of quartz lenses and irregular bodies in faults, drag folds, ruptured and sheared axes of isoclinal folds, and other structures. These contain essentially quartz with small amounts of pyrite, sphalerite, galena, pyrrhotite, arsenopyrite, scheelite, and gold. Two or more generations of quartz may occur in the lenses. The sulfides are generally later than the quartz, but there is relatively little age difference between the various sulfides. Most of the quartz bodies have no well-developed alteration zones, but a few are marked by a narrow zone of tourmalinized and sericitized rock.

3. Formation of late faults and fractures followed by deposition of quartz lenses and "giant quartz veins." These are the same age as those in the greenstone belt and are identical in most respects.

SULFUR ISOTOPE VARIATIONS IN NATURE

The pioneer work of Thode, Macnamara, and Collins (23), Macnamara and Thode (16), Macnamara, Fleming, Szabo, and Thode (17), Thode, Macnamara, and Fleming (24) and Thode, Wanless, and Wallouch (25) has shown that considerable variation exists in the sulfur isotope distribution in nature. Tudge and Thode (26) and Sakai (21) have determined the partition function ratios of some isotopic molecules of sulfur and have calculated the fractionation factors for certain exchange reactions at various temperatures. The overall isotopic variation between $SO_4^= \rightleftarrows H_2S$ is calculated to be 7.4 percent at 25° C, decreasing to about 1 percent at 500° C. Generally speaking, one finds a variation of this order of magnitude in nature with the heavier sulfur isotope, sulfur-34, concentrated in sulfate minerals and in sea water whereas the lighter isotope, sulfur-32, is enriched in sedimentary sulfides. Analyses of meteoritic troilite (16) have failed to reveal any variations within the precision of the results and, consequently, the determined S^{32}/S^{34} ratio of 22.22 has been adopted as the standard for all sulfur isotope studies.

The range of the isotopic results reported by Thode (23), Ault, and Kulp (1), and others is illustrated in Figure 2. The meteoritic standard has been assigned a value of zero and results plotted below the zero line have positive values indicating that they contain more S^{34} than the meteoritic standard, while results appearing above the zero line are enriched in S^{32}. It will be noted that sea water sulfate has a very uniform isotopic ratio (1) indicated by the dashed line.

The Yellowknife results reported in this paper fall within a narrow range close to the meteoritic value. The total range of the isotopic distribution for 140 sulfide samples from the region is only 1.5 percent with the average value falling slightly below meteoritic, at + 2.2‰. The majority of the results fall within the narrow limits + 0.5 to + 4.0‰ indicated by the solid bar. Only six samples have ratios lighter than meteoritic, and two others have an isotopic composition identical with the standard. Prior to the de-

velopment of mass spectrometric apparatus employing specialized methods of sample introduction and simultaneous ion beam collection (18, 27), it would have been impossible to distinguish between results falling within such narrow limits, and one would have been forced to the conclusion that the isotopic distribution was constant throughout the district.

In addition to the sulfides, four sulfate samples separated from the mine waters were analyzed. The sulfate sulfur values, ranging from +9 to +26‰, are all considerably heavier than the sulfides.

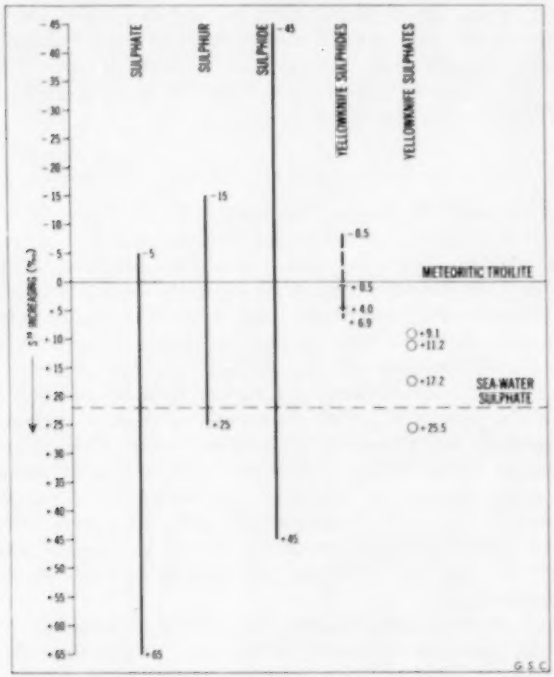

FIG. 2. Sulfur isotope distribution in nature.

SULFUR ISOTOPE DISTRIBUTION IN COUNTRY ROCKS OF GREENSTONE BELT

The sulfur isotope values are presented in accordance with the time sequence of geologic events as outlined under the general geology and mineralization of the district. The significance and interpretation of the observed trends will, in general, be reserved for the concluding sections.

Granitic Rocks (Granodiorite and Quartz-feldspar Porphyry)

The sulfur isotope ratios determined for the granitic rocks west of Yellowknife Bay are given in Table 1. The value for the western granodi-

TABLE 1

GRANITIC ROCKS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
91	Py from granodiorite*	Western granodiorite.	+5.0
356	Py from fresh porphyry. Exposed dike.*	300' level Negus mine.	+6.8
400	Py from porphyry. Exposed dike.*	Negus mine.	+3.1
342	Py from porphyry. Exposed dike.*	Rycon mine.	+2.9
65	Py from quartz-feldspar porphyry. All bodies.*	Rycon, Con, and Negus mine areas.	+3.1
		Average of porphyry	+4.0

*Represents composite chip sample in all tables.

Symbols in all tables.. Py, pyrite; pyrr, pyrrhotite; asp, arsenopyrite; sulfo, sulfosalts; sp, sphalerite; cp, chalcopyrite; td, tetradhedrite; sb, stibnite; gn, galena.

TABLE 2

GREENSTONE BELT ROCKS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
87	Py from amphibolite facies. All traverses across facies.*	Greenstone belt.	+1.9
86	Py from epidote amphibolite facies. All traverses across facies.*	Greenstone belt.	+1.1
84	Py from epidote amphibolite facies, across 1500'.*	Southeast of Stock Lake	+1.6
118	Py from epidote amphibolite facies, across 50'.*	Negus-Rycon system adjacent to Negus mine.	+1.1
123	Py from epidote amphibolite facies, across 250'.*	Campbell system. Adjacent to Negus mine.	+0.6
362	Py from epidote amphibolite facies (Slightly chloritized), across 100'.*	Giant system. Adjacent to 425' level, Giant mine.	+1.6
357	Py from epidote amphibolite facies, across 20'.*	Giant system adjacent to Giant mine	+1.3
104	Py from epidote amphibolite facies, across 100'.*	Giant system, adjacent to Akaitcho mine.	+2.2
	Average of epidote amphibolite facies (7 samples)		+1.4

TABLE 3

TUFFS

A) GRAPHITIC

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
37	Massive py associated with large amounts of graphite[1].	Ranney tuff, west of Giant mine.	+5.0
38	Massive pyrr associated with No. 37[1].	Ranney tuff, west of Giant mine.	+2.0
27	Py associated with pyrr in graphitic bed[1].	Giant mine.	+2.7
33	Pyrr associated with No. 27[1].	Giant mine	+2.4
101	Py in graphitic tuff[1].	Akaitcho mine area.	+3.3
345	Py in graphitic banded tuff[1].	Lynx area 1/2 mile north of No. 101.	+5.6
		Average	+3.5

B) SILICEOUS

116	Py in cherty bands in tuff. No graphite.	A.E.S. tuff, west of Akaitcho area	-0.9
349	Py in chloritized tuff.	A.E.S. tuff, west of Akaitcho area.	-0.3
35	Py with pyrr and magnetite[2].	Ranney tuff, David Lake.	-2.7
36	Pyrr with magnetite[2].	Ranney tuff, David Lake.	-0.9
		Average	-1.2

[1] Average carbon content 1.28%
Average sulphur content 1.45%

[2] Average carbon content 0.10%
Average sulphur content 0.1 to 0.5%

orite (No. 91) was obtained from a composite sample composed of fresh chips collected west of the granodiorite-greenstone contact over a distance of some fifteen miles and, therefore, represents an average isotope distribution for a very large volume of rock. The isotopic result, + 5‰, indicates that the granodiorite contains more S^{34} than the meteoritic standard. The quartz-feldspar porphyries also contain sulfur enriched in S^{34}, and in one instance (No. 356) the sulfides of a porphyry contain more S^{34} than found in the sulfides of the western granodiorite.

Greenstones

Proceeding east from the granodiorite-greenstone contact composite samples of fresh rock were taken on traverses across the amphibolite and

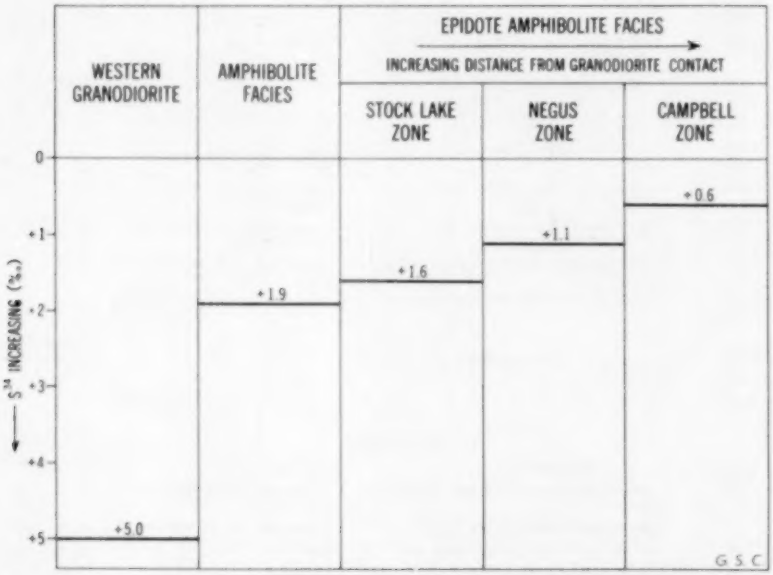

FIG. 3. Sulfur isotope distribution in granodiorite and metamorphic facies of greenstone belt.

epidote amphibolite facies throughout the length of the greenstone belt. From the sulfur isotope ratios given in Table 2, it is apparent that sulfide minerals of the greenstone rocks contain much less S^{34} than those found in the western granodiorite and quartz-feldspar porphyries. Furthermore, it will be noted that the value for the amphibolite facies (No. 87) is + 1.9‰ which is heavier than the average of + 1.4‰ determined for seven samples collected from the epidote amphibolite facies. With the exception of the single sample

from the Akaitcho mine (No. 104) all of the epidote amphibolite samples contain less S^{34} than the composite from the amphibolite facies.

The isotopic values are plotted according to the geographical location of the samples in Fig. 3. It is immediately apparent that a correlation exists between the sulfur isotope ratio and the distance from the granodiorite-greenstone contact. While the differences between the zones of the epidote amphibolite facies and the amphibolite facies are small, a major break in the isotope ratio occurs between the amphibolite facies and the western granodiorite. This is analogous to the break observed in the geochemical profiles at this contact (4).

Tuffs

The isotope values determined for ten samples of tuffaceous sediments are presented in Table 3. All of the graphitic types are enriched in S^{34}, whereas the values determined for the siliceous tuffs are all very close to the meteoritic standard. The explanation of this marked difference is obscure, but the high carbon content (Table 3) in the graphitic tuffs suggests that life processes may have been involved.

SULFUR ISOTOPE DISTRIBUTION IN DEPOSITS OF GREENSTONE BELT

Early Pre-ore Quartz Lenses in Tension Fractures

The formation of quartz lenses in tension fractures in the country rocks represents the first stage in the mineralization of the greenstone belt. As noted above, geochemical studies indicate that the fractures have been filled as the result of a transfer of silica from the wall rocks into the tension fractures. In Table 4 the isotope values determined for samples from two such quartz lenses are compared with the average value for the epidote amphibolite facies of the greenstone belt. In both cases, the lighter sulfur isotope has been concentrated in the fractures, indicating a preferential movement of the lighter isotope into the low pressure zones produced when the fractures were formed. The isotopic results would, therefore, appear to corroborate the secretion hypothesis postulated on the evidence from silica profiles (5).

Deposits in Transecting Shear Zones

The Con System.—Thirteen composite ore samples collected from the 250 to the 2,300-foot level of the Con mine have been analyzed isotopically. Three things are apparent from the results given in Table 5: 1) the ore contains considerably more S^{34} than reported for the greenstone rocks; 2) there is relatively little variation from level to level; 3) there is no evidence of a relationship between isotopic distribution and depth in the mine.

The Con mine is situated in that part of the epidote amphibolite facies represented by the Stock Lake analysis (Table 2, Fig. 3) for which a value of + 1.6‰ was obtained. The average value for the sulfide ore of the Con mine is + 3.8‰, indicating an increase of 2.2‰ over the associated country rock.

TABLE 4

EARLY PRE-ORE QUARTZ LENSES IN TENSION FRACTURES

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}(‰)$
	Epidote amphibolite facies[1].	Greenstone belt	+1.4
114	Py in isolated tension fractures.*	North of Abaitcho fault	+0.3
144	Py in carbonate-epidote stringers, possibly pre-ore.	Associated with Campbell shear zone system, Negus mine.	+0.6

[1]Average of epidote amphibolite facies, see Table 2.

TABLE 5

CON SYSTEM - ORE - DEPTH PROFILE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}(‰)$
171	Py, asp, minor sulfs. Lens along 300°.*	250' level, shear C-4.	+4.2
174	Py, asp, minor sulfs. Lens along 150°.*	375' level, shear C-4.	+3.3
173	Py, asp, minor sulfs. Lens along 150°.*	500' level, shear C-4.	+6.2
177	Py, asp, minor sulfs. Lens along 250°.*	650' level, shear C-4.	+2.4
179	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 100°.*	800' level, shear C-4.	+3.1
180	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 200°.*	950' level, shear C-34.	+4.0
181	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 300°*.	1,100' level, shear C-4	+3.8
183	Py, asp, minor sulfs. Ore in silicified sericite schist. Lens along 150°.*	1,250' level, shear C-34.	+3.6
187	Py and sulfs in grey, cherty replacement quartz. Lens along 25°.*	1,400' level, shear C-4.	+3.1
188	Py, asp, minor sulfs. Quartz-sericite schist, along 25° band.*	1,550' level, shear C-4.	+4.2
189	Py, asp, minor sulfs in quartz-carbonate-sericite schist. Along 350°.*	1,850' level, shear C-4	+2.9
190	Py in silicified sericite schist.	2,300' level, shear C-4	+4.3
191	Py in low-grade gold quartz ore.	2,300' level, shear C-4	+3.8
		Average	+3.8

TABLE 6

NEGUS-RYCON SYSTEM - ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}(‰)$
117	Td in gold-quartz lens.	Surface, Negus-Rycon system.	+1.8
131	Py, asp, sulfs. Lens along 60°.*	100' level N-15 stope, Negus mine.	+2.7
53	Sb and minor sulfs.*	100' level, N-3 shear, Negus mine.	+0.2
132	Py, asp, sulfs. Lens along 110°*.	200' level N-15 stope, Negus mine.	+1.8
44	Sb and minor sulfs.*	225' level, R-54 shear, Rycon mine.	+1.1
133	Py, asp, sulfs. Lens along 100°.*	300' level N-15 stope, Negus mine.	+2.2
122	Py in quartz lens.*	300' level N-15 stope, Negus mine.	+1.6
134	Py, asp, sulfs. Lens along 70°.*	425' level N-15 stope, Negus mine.	+2.4
351	Py in mottled to black quartz. Lens along 40°.*	425' level N-3 shear, Negus mine.	+2.0
30	Sb and minor sulfs.*	450' level R-57 shear, Rycon mine.	+2.7
135	Py, asp, sulfs. Lens along 100°.*	550' level N-15 stope, Negus mine.	+0.7
137	Py, asp, sulfs. Lens along 80°.*	675' level N-15 stope, Negus mine.	+2.0
52	Massive py in gold quartz lens. Chip sample	675' level N-3 shear, Negus mine.	+0.4
51	Sp in gold quartz lens.*	675' level N-3 shear Negus mine.	+3.3
45	Sb and minor sulfs.*	800' level, Rycon mine.	+1.3
138	Py, asp, sulfs. Lens along 110°.*	800' level N-15 stope, Negus mine.	+1.3
139	Py, asp, sulfs. Lens along 80°.*	979 level N-15 stope, Negus mine.	+1.1
141	Py, asp, sulfs. Lens along 80°.*	1,100' level N-15 stope, Negus mine.	+0.7
142	Py, asp, sulfs. Lens along 20°.*	1,250' level N-15 stope, Negus mine.	+1.8
	Average	Total	+1.7
	Average	Less late minerals (Samples 117, 53, 44, 30, 45)	+1.9

The Negus-Rycon System.—A total of nineteen ore samples, listed in Table 6, were studied from the Negus-Rycon system. The ore in this system contains sulfur considerably lighter (+ 1.7‰) than that found in the Con mine (+ 3.8‰), but heavier than the neighboring epidote amphibolite facies (+ 1.1‰).

Ten of the samples were taken between the 100- and 1,250-foot levels of the N-15 stope, of the Negus mine. The results, given in Table 7, show no systematic variation with depth.

The Giant-Campbell System.—The isotope values determined for twelve samples from mines and prospects in the Giant-Campbell system are given in

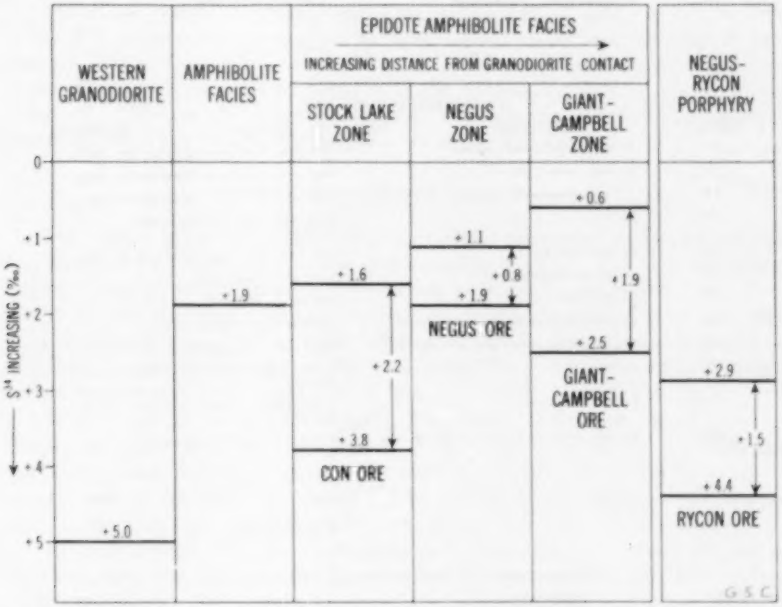

FIG. 4. Sulfur isotope distribution in gold-quartz deposits of greenstone belt.

Table 8. A rather large spread exists between the samples studied, but the average value of + 2.5‰ is again heavier than the value of + 0.6‰ determined for the associated epidote amphibolite facies of the Campbell zone.

The average results for the three systems are combined with the analyses of the country rock in Figure 4. With the exception of the Negus mine, the sulfur isotope ratios determined for the ore zones exhibit the same correlation with distance from the granite contact observed in the case of the metamorphic facies. This indicates to us that the individual orebodies contain sulfides derived by diffusion from their associated country rock and that the amount of enrichment over the country rock base level is of the same

TABLE 7

DEPTH PROFILE NEGUS MINE, NEGUS-RYCON SYSTEM - ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
131	Py, asp, sulfs. Lens along 60°.*	100' level N-15 stope.	+2.7
132	Py, asp, sulfs. Lens along 110°.*	200' level N-15 stope.	+1.8
133	Py, asp, sulfs. Lens along 100°.*	300' level N-15 stope.	+2.2
134	Py, asp, sulfs. Lens along 70°.*	425' level N-15 stope	+2.4
135	Py, asp, sulfs. Lens along 100°.*	550' level N-15 stope.	+0.7
137	Py, asp, sulfs. Lens along 80°.*	675' level N-15 stope.	+2.0
138	Py, asp, sulfs. Lens along 110°.*	800' level N-15 stope.	+1.3
139	Py, asp, sulfs. Lens along 80°.*	975' level N-15 stope.	+1.1
141	Py, asp, sulfs. Lens along 80°.*	1,100' level N-15 stope.	+0.7
142	Py, asp, sulfs. Lens along 20°.*	1,250' level N-15 stope.	+1.8
		Average	+1.7

TABLE 8

GIANT-CAMPBELL SYSTEM - ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
361	Py in silicified sericite schist.*	100' level Giant mine, Giant system.	+3.6
365	Py, asp, minor sulfs.*	425' level, Giant mine, Giant system.	+2.4
105	Py, asp, minor sulfs.*	310 stope Giant mine, Giant system.	+2.2
108	Py.*	Brock shear zone. Surface, Giant system.	+2.4
107	Sp, late stage.*	306 stope, Giant mine, Giant system.	+0.4
50	Sb and minor sulfs in vugs.*	Giant mine, Giant system	+0.3
39	Gn, late stage.	306 stope, Giant mine.	0.0
102	Py, asp, minor sulfs. Split core sample.	Akaitcho mine, Giant system.	+3.1
110	Py, asp, minor sulfs. Split core sample.	Lynx claim, Giant system.	+2.4
109	Py.*	North of Lynx claim.Surface. Giant system.	+1.9
126	Py, asp, minor sulfs.*	1, 300' level Negus mine, Campbell system.	+1.3
369	Py, asp, minor sulfs. Lens along 500'.*	2, 750' level Con Mine, Campbell system.	+3.6
	Average	Total	+2.0
	Average	Lens late minerals (Samples 107, 50, 39)	+2.5

TABLE 9

PARALLEL SHEAR ZONE SYSTEMS - MINERALIZED ZONES AND ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
350	Cp and sulfs in quartz lens-ore.*	A.K.S. system, Gar Lake. Surface.	+3.2
113	Py in quartz lens-ore.*	Ranney system, Between West Bay and Akaitcho faults.	+2.9
112	Py in quartz lens-ore.*	Ranney system north of Akaitcho fault.	+0.9
54	Sp and Sb.*	Ranney system, south of Crestaurum mine.	0.0
398	Py, sulfs, sb and sp in silicified ore.*	Crestaurum system.	+2.2
399	Massive sb in ore.	Crestaurum system.	+1.6
46	Sp in ore, age uncertain, probably ore stage.	Crestaurum system.	+3.6
47	Late gn and sp.	Crestaurum system.	+0.9
395	Py in quartz lens.*	Kam Point system. Surface.	+3.6
394	Cp in quartz lens.*	Kam Point system. Surface.	+3.3
	Average	Total	+2.2
	Average	Lens late minerals (Samples 54, 399, 47)	+2.8
	Average py - asp ore - Ranney-Crestaurum system		+2.4

order of magnitude in each shear zone system. The inconsistency observed in the Negus mine is believed attributable to a high abundance of paragenetically late minerals (See below).

In addition, the results obtained for the sulfides of the Negus-Rycon porphyry and the associated Rycon ore (No. 392 Table 1 and No. 366 Table 10) are illustrated in Figure 4. It will be noted that the sulfide ore is 1.5‰ heavier than the sulfides of the porphyry, an increase essentially in agreement with that reported for the Con and Giant-Campbell ores.

Deposits in Parallel Shear Zones

These shear zone systems parallel the strike and in many cases the dip of the lava flows. All shear zones sampled lie within the epidote amphibolite facies. Ten samples, taken from the A.E.S., Ranney, Crestaurum, and Kam Point systems, have been analyzed and the values determined are listed in Table 9. The average value of + 2.8‰ is again heavier than any of the ratios obtained for the epidote amphibolite facies (Table 2).

Profiles Across Major Shear Zones

The major gold-quartz orebodies and their associated alteration haloes are localized in shear zones in the greenstone belt (Fig. 1). The alteration haloes comprise a carbonate-sericite schist zone adjacent to the orebodies, which grades through a chlorite-carbonate or chlorite schist zone into the epidote amphibolite country rock. The widths of the alteration zones are variable; in places they are a few inches to a few feet in width, in other places they extend over hundreds of feet.

Where possible, composite samples representing the country rock, chlorite schist, carbonate-sericite schist, and the ore, were collected in sequence on particular mine levels, to determine whether or not an isotopic variation existed across the alteration zones. The results of eighteen profiles across both transecting and parallel systems are given in Tables 10 and 11.

In some instances, it was impossible to separate the two phases of alteration and only one isotope determination has been reported. The description indicates whether the sample represents a combination of both the chlorite and the carbonate-sericite schist or only the carbonate-sericite schist. In some shear zones it was impossible to obtain samples from the associated epidote amphibolite country rock. In such cases, the average value for the epidote amphibolite facies (+ 1.4‰) was used for comparison.

From an examination of the values obtained for the profiles, it is evident that: 1) without exception, in the eighteen cases considered, the ore contains more S^{34}—i.e. is heavier—than the associated epidote amphibolite country rock; 2) in twelve instances, the sulfur in the ore is also heavier than the sulfur in the alteration zones; 3) in five of the six cases in which the sulfur in the ore is lighter than the associated sulfur in the alteration zone, the value for the ore is within 10 percent of the heaviest member of the alteration zone.

TABLE 10

PROFILES OF TRANSECTING SYSTEMS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$(‰)
Con system - Profile 1			
	Epidote amphibolite facies.[1]	Greenstone belt	+1.4
372	Py and asp in sericite schist. Along 300'.*	250' level Con mine. Shear C-4.	+3.6
371	Py, asp, sulfs - ore. Lens along 300'.*	250' level Con mine. Shear C-4	+4.2
Con system - Profile 2			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
375	Py and asp in sericite schist. Along 250'.*	650' level, Con mine. Shear C-4.	+2.0
377	Py, asp, sulfs - ore. Lens along 250'.*	650' level Con mine. Shear C-4.	+2.4
Con system - Profile 3			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
378	Py, asp in sericite schist. Along 20'.*	800' level Con mine. Shear C-4.	+3.3
379	Py, asp, sulfs-ore. Lens along 100'.*	800' level Con mine. Shear C-4.	+3.1
Con system - Profile 4			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
382	Py and asp in silicified sericite schist. Lens along 200'.*	1,100' level Con mine. Shear C-4.	+4.2
381	Py, asp and sulfs in quartz-sericite schist-ore. Along 300'.*	1,100' level Con mine. Shear C-4.	+3.8
Con system - Profile 5			
	Epidote amphibolite facies[1].	Greenstone belt	+1.4
385	Py and minor asp. Average of two samples of chlorite carbonate and chlorite-carbonate-sericite schist. Along 50'.*	1,400' level Con mine. Shear C-4.	+1.1
386	Py and asp in carbonate-sericite schist. Along 20'.*	1,400' level Con mine. Shear C-4	+2.4
387	Py and sulfs in grey cherty replacement quartz lens. Lens along 25'.*	1,400' level Con mine. Shear C-4	+3.1
Negus-Rycon system - Profile 1			
118	Py in epidote amphibolite facies. Across 50'.*	Negus-Rycon system, 300' level Negus mine.	+1.1
119	Py in chlorite schist. Across 1'.*	Negus-Rycon system, 300' level Negus mine.	+2.0
121	Py and asp in carbonate sericite schist. Across 1'.*	Negus-Rycon system, 300' level Negus mine.	+2.2
122	Py in quartz lens adjacent to No. 121. - ore.*	Negus-Rycon system, 300' level Negus mine.	+3.6
Negus-Rycon system - Profile 2			
	Epidote amphibolite facies[1].	Greenstone belt	+1.4
353	Py and pyrr in chlorite schist. Across 6".*	Negus-Rycon system, 425' level Negus mine.	+1.8
352	Py and asp in sericite-carbonate schist. Across 2".*	Negus-Rycon system, 425' level Negus mine.	+1.6
351	Py in mottled to black quartz lens - ore. Lens along 40'.*	Negus-Rycon system, 425' level Negus mine.	+2.0

Table 10 - cont'd.

Negus-Rycon system - Profile 1			
192	Porphyry. Exposed dike.*	Rycon mine.	+2.9
63	Quartz feldspar porphyry. All bodies.*	Rycon, Con, and Negus mine areas.	+3.1
167	Disseminated py in sericitized porphyry.	5th level Rycon mine.	+4.9
166	Disseminated py in grey quartz adjacent to No. 167.	5th level Rycon mine.	+4.4
Campbell system - Profile 1			
123	Py in epidote amphibolite facies. Across 250'.*	Campbell system, 1, 300' level Negus mine.	+0.6
124	Py in chlorite schist. Across 50'.*	Campbell system, 1, 300' level Negus mine.	+1.3
125	Py in carbonate-sericite schist. Across 3'.*	Campbell system, 1, 300' level Negus mine.	+1.1
126	Py, asp, sb and sulfs in quartz lens-ore.*	Campbell system, 1, 300' level Negus mine.	+1.3
Giant system - Profile 1			
157	Py in chloritized epidote amphibolite facies. Across 20'.*	Giant system, 100' level Giant mine.	+1.3
158	Py in chlorite schist. Across 40'.*	Giant system, 100' level Giant mine.	+2.2
159	Py in chlorite-carbonate-sericite schist. Across 20'.*	Giant system, 100' level Giant mine.	+3.3
161	Py in silicified sericite schist-ore.*	Giant system, 100' level Giant mine.	+3.6
Giant system - Profile 2			
162	Py in chloritized epidote amphibolite facies. Across 100'.*	Giant system, 425' level Giant mine.	+1.6
163	Py in chlorite schist. Across 100'.*	Giant system, 425' level Giant mine.	+3.6
164	Py in carbonate-sericite schist. Across 20'.*	Giant system, 425' level Giant mine.	+2.9
165	Py, asp, sulfs-ore.*	Giant system, 425' level Giant mine.	+2.6
Giant system - Profile 3			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.6
106	Py and asp in chlorite and chlorite-carbonate schist.*	Giant system, 310 stope Giant mine.	+1.6
105	Py, asp, sulfs. Ore.*	Giant system, 310 stope Giant mine.	+2.2
Giant system - Profile 4			
104	Py in epidote amphibolite facies. Split drill core across 100'.	Giant system, Akaitcho mine.	+2.2
103	Py in chlorite and chlorite-sericite schist. Split drill core across 40'.	Giant system, Akaitcho mine.	+1.8
102	Py, asp, and sulfs-ore. Split drill core.	Giant system, Akaitcho mine.	+3.1
Handle Lake system			
147	Asp in aplite wall rock.	Handle Lake system.	+1.9
146	Asp in gold-quartz ore.	Handle Lake system.	+1.3
Fox Lake area			
87	Amphibolite facies. Composite.	Greenstone belt.	+1.9
148	Py in shear zone and quartz lens cutting amphibolite facies.	Fox Lake area.	+2.0
Octopus Lake area			
	Average of epidote amphibolite facies.[1]	Greenstone belt.	+1.4
264	Py in gold-quartz veins.	Octopus Lake area.	+2.7

[1]Average of epidote amphibolite values, see Table 2.

TABLE 11

PROFILES OF PARALLEL SYSTEMS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}_{(Sp.)}$
A.E.S. system			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
347	Py in chlorite schist minor asp.	A.E.S. system, Gar Lake.	+3.1
346	Py in carbonate-sericite schist.	A.E.S. system, Gar Lake.	+1.6
350	Cp and sulfs in quartz lens-ore.	A.E.S. system, Gar Lake.	+1.2
Crestaurum system			
	Epidote amphibolite facies.[1]	Greenstone belt.	+1.4
196	Py in chlorite schist.*	Crestaurum system.	+1.8
197	Py in sericite schist.*	Crestaurum system.	+2.3
198	Py, sulfs, sb, and sp in silicified ore.*	Crestaurum system.	+2.2

[1]Average of epidote amphibolite values, see Table 2.

For purposes of illustration, an average has been taken of eight of the profiles which are complete, i.e. comprise four members. The averages are plotted in Figure 5. While there are some reversals between the zones in the individual profiles, the averages fall in a steady progression from the country rock, through the alteration halo, to the ore zone, with the heavier sulfur concentrated in the ore. This progression holds in the transecting systems, the parallel systems, in the Rycon porphyry, and in isolated shear zones such as those in the Handle Lake, Fox Lake, and Octopus Lake areas. It would seem to follow, therefore, that the sulfur in the ore bears a consistent relationship to the sulfur in the associated country rock as suggested previously and as shown in Figure 4.

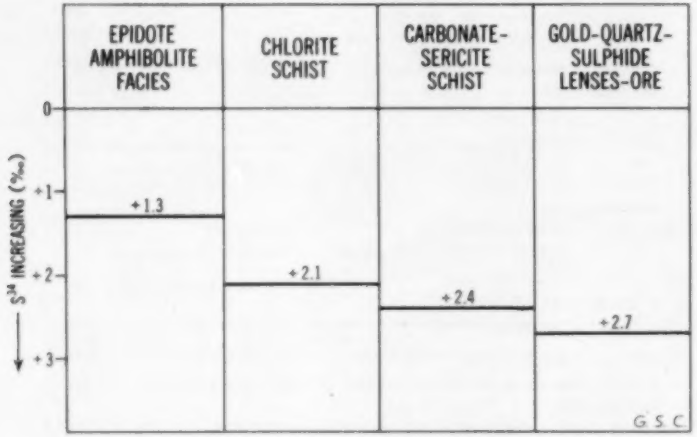

FIG. 5. Sulfur isotope distribution in alteration zones.

Paragenetic Relationships

Detailed studies (5, 9, 10) have shown that the sulfosalts, stibnite, and galena are paragenetically later than pyrite and arsenopyrite in all orebodies. In some instances, it has been possible to separate the late sulfides from the early pyrite and arsenopyrite, whereas in other cases, as in the Negus-Rycon system, for example, the desired separation was not possible.

A comparison of the sulfur isotope distribution in the early and late sulfides is given in Table 12. In all systems, the average value for the early pyrite and arsenopyrite in the ore is heavier than the average of the late sulfosalts, stibnite, and galena. The differences are most marked in the Giant-Campbell and the Ranney-Crestaurum systems where a complete separation of early and late minerals was achieved. It is apparent that the minerals formed late in the mineralization sequence have concentrated the lighter sulfur isotope, S^{32}.

TABLE 12

SULPHOSALTS, STIBNITE, AND GALENA

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
Giant-Campbell system			
50	Sb and minor sulfs in vugs.*	Giant mine.	+0.3
107	Sp, late stage.*	306 Stope, Giant mine.	+0.4
39	Gn, late stage.	306 Stope, Giant mine.	0.0
		Average	+0.2
		Average of py-asp ore[1]	+2.5
Kenney-Crestaurum system			
54	Sp and sb.*	Kenney system, south of Crestaurum mine.	0.0
399	Massive sb in ore.	Crestaurum system.	+1.6
47	Late gn and sp.	Crestaurum system.	+0.9
		Average	+0.8
		Average of py-asp ore[2]	+2.4
Negus-Rycon system			
117	Td in gold-quartz lens.	Surface.	+1.8
53	Sb and minor sulfs.*	100' level, N-3 shear Negus mine.	+0.2
44	Sb and minor sulfs.*	225' level R-54 shear, Rycon mine	+1.1
30	Sb and minor sulfs.*	450' level, R-57 shear, Rycon mine.	+2.7
45	Sb and minor sulfs.*	800' level, Rycon mine.	+1.3
	[1]See Table 8 [2] " " 9 [3] " " 6	Average	+1.4
		Average py-asp ore[3]	+1.9

TABLE 13

SECOND STAGE QUARTZ-CARBONATE LENSES - POST-ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
41	Asp in cross-cutting post-ore stringer.	2, 300' level Con mine, Campbell system.	+0.7
32	Cp in post-ore quartz-carbonate lens.	2, 600' level Con mine, Campbell system.	+1.6
48	Sp in post-ore fracture.	1, 300' level Negus mine, Campbell system.	+0.9
49	A p in cross-cutting quartz-carbonate lens.	1, 300' level Negus mine, Campbell system.	+0.2
63	Gn, late stage.	800' level Con mine, Con system.	+1.3
39	Gn, late stage.	Giant mine, 306 stope, Giant Campbell system.	0.0
	Average		+0.8
	Average of py-asp ore - Giant Campbell system[1]		+2.5
	Average of py-asp ore - Con system[2]		+3.8
	[1]See Table 8 [2] " " 5		

TABLE 14

SULPHIDES IN SECOND STAGE QUARTZ-CARBONATE LENSES COMPARED WITH THOSE IN ASSOCIATED ORE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
49	Asp in cross-cutting quartz-carbonate lens.	1, 300' level Negus mine, Campbell system.	+0.2
126	Py, asp, minor sulfs in ore.	1, 300' level Negus mine, Campbell system.	+1.3
41	Asp in cross-cutting post-ore stringer.	2, 300' level Con mine, Campbell system.	+0.7
391	Py and asp in low grade gold-quartz ore.	2, 300' level Con mine, Campbell system.	+3.8

Post-ore Quartz-carbonate Lenses

Isolated quartz-carbonate lenses, with no associated alteration haloes, cut the ore zones of the major shear zone systems. They appear to have formed as a result of the development of dilatant zones into which material moved from the surrounding rock.

The sulfur isotope values determined for samples taken from six lenses of this type are compared, in Table 13, with the average results for the sulfide ore in the corresponding systems. The sulfides in the late lenses are consistently lighter, indicating that the lighter sulfur isotope was more mobile under the influence of the pressure gradients developed in the dilatant zones.

In some instances, it has been possible to compare the sulfur isotope ratios of sulfides in late lenses with sulfide ore in close proximity to the lenses on the same level of a mine. Two examples are given in Table 14 indicating the magnitude of the isotopic fractionation resulting from diffusion of sulfur to its present site.

The Effect of the Diabase Dikes

Diabase dikes cut the orebodies at several places. Two occurrences, one on the 375-foot level of the Con system, and the other on the 2,750-foot level of the Campbell system, were sampled in detail to test the hypothesis that the temperature gradient associated with the cooling of the molten dike modified the existing sulfur isotope distribution. As shown in Table 15 and Figure 6, the effect was indeed dramatic. The sulfide minerals adjacent to the dike have been markedly enriched in S^{34} with respect to the associated ore on the same level of the mine, indicating that the lighter isotope has been preferentially expelled from the region of higher temperature.

The amphibolite facies adjacent to the western granodiorite contains sulfides which are heavier than those of the lower grade facies. In this respect, the metamorphic effect of the western granodiorite on the greenstone rocks is analogous to the effect of the temperature gradient on the adjacent sulfide ore during the cooling of the diabase dike.

Late Faults and Fractures

Seven samples from late faults and fractures were analyzed and the results are recorded in Table 16. In this group extremes ranging from + 6.6‰ to − 8.5‰ are represented with a fairly even distribution over the intermediate range. No explanation is advanced for this divergence except to suggest that each is the result of localized processes that may or may not be related to the general sulfur isotope distribution of the region.

Sulfates in Underground Waters

Four sulfate samples extracted from underground waters flowing from fractures and faults were analyzed yielding the results given in Table 17. During the first stages of the study sulfates were converted directly to SO_2 for mass spectrometric analysis, thereby eliminating the chemical conversion

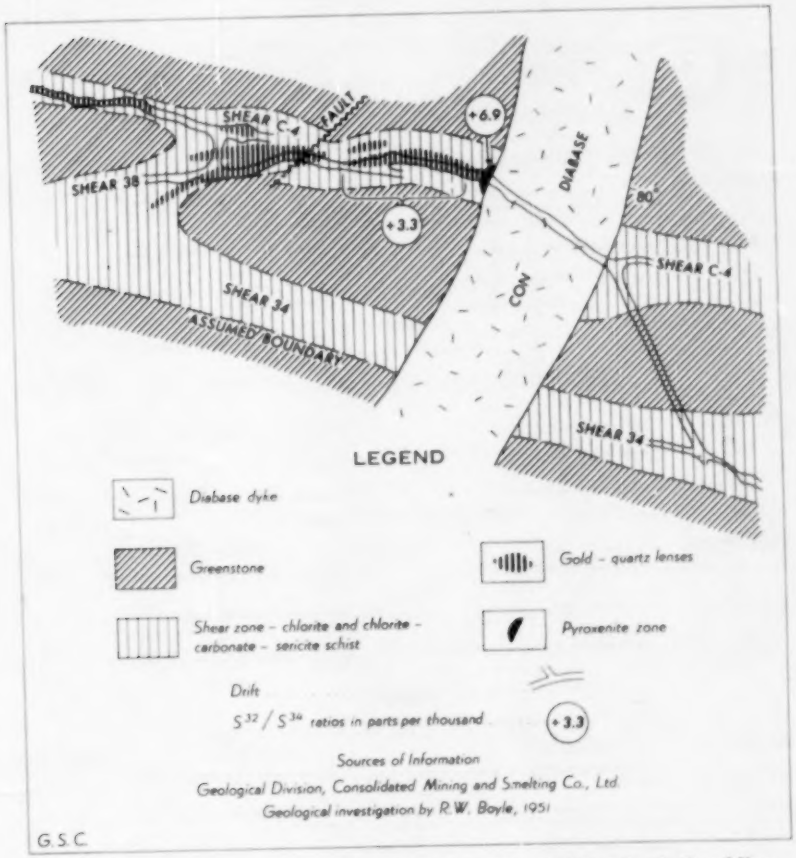

FIG. 6. Plan of geology in vicinity of diabase dike, 375 foot level, Con Mine, Con System.

from sulfate to sulfide and any possible laboratory isotope fractionation. Experience has shown, however, that reproducible results are not obtained by this procedure, and a method whereby the sulfates are converted to Ag_2S or CdS, has been adopted.

While the precision of the results for the direct conversion of $BaSO_4$ is not as high as for the conversion of the sulfides, nevertheless, the values show that all the underground waters are greatly enriched in S^{34} with respect to the sulfides in the region, and in one instance the water contains more S^{34} than sea water sulfate.

Other work (5) has suggested that the underground waters are derived from surface lakes and ponds overlying the shear zones. In these bodies

TABLE 15

EFFECT OF DIABASE DIKE - CON MINE

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
Shear C-4, Con system			
374	Py, asp, sulfs. Lens along 150'.*	375' level. 100' southwest of diabase dike contact.	+3.3
262	Py from pyroxenite alteration zone.	375' level. Adjacent to dike contact.	+6.9
Campbell system			
369	Py, asp, sulfs. Lens along 500'.*	2, 750' level. 500' south of dike contact.	+3.6
263	Py in quartz lens.*	2, 750' level. 25' south of dike contact.	+3.8
368	Py.*	2, 750' level. In shear adjacent to diabase contact.	+4.2

TABLE 16

LATE FAULTS AND FRACTURES

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
Late faults			
89	Py in late fault.*	Pud fault, Sand Lake area.	+2.9
127	Crystals of py associated with calcite.	Negus fault, 225' crosscut, Negus mine.	+1.8
88	Cp in white calcite.	Townsite fault, Latham Island.	+0.3
22	Cp in quartz.	Akaitcho fault.	-6.5
Late fractures			
24	Py in late fracture.	300' level Negus mine, Negus-Rycon system.	+6.6
23	Py in late slip.	425' level Negus mine, Negus-Rycon system.	-0.2
370	Sp in axinite vein cutting late diabase dike.	2, 300' level, Con mine, Campbell system.	+1.1

TABLE 17

UNDERGROUND WATERS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}$ (‰)
151	Sulfates precipitated from water issuing from Negus fault.	Negus mine, Campbell system.	+17.2[1]
454	Sulfates precipitated from water from fracture associated with West Bay fault.	2, 300' level Con mine, Campbell system.	+ 9.1[2]
193	Sulfates from carbonate stalactite and stalagmite associated with 459.	2, 300' level Con mine, Campbell system.	+11.2[1]
460	Sulfates precipitated from saline water flowing from fracture.	2, 300' level Con mine, Con system.	+25.5[3]

[1]Sulfur dioxide produced directly from $BaSO_4$. See text.
[2]Sample converted to Ag_2S for conversion to SO_2.
[3]Sample converted to CdS for conversion to SO_2.

TABLE 18

YELLOWKNIFE SEDIMENTS - COUNTRY ROCKS

SAMPLE	DESCRIPTION	LOCATION	% CARBON	% SULPHUR	$\delta S^{32}/S^{34}$ (‰)
96	Py from greywacke, arkose and quartzite samples[1].	Burwash area, relatively unmetamorphosed zone.	0.13	0.13	+1.6
92	Py from graphitic slate and argillite samples[2].	Burwash area, relatively unmetamorphosed zone.	0.30	0.68	+3.6
393	Py from four skarn lenses.*	Prosperous Lake area, in hornfels and highly metamorphosed zone.	trace to 0.10	0.10	+3.6
	Weighted average greywacke to slate 10:1				+1.8

[1]Composite sample of approximately 70 specimens and chips from Yellowknife sediments.

[2]Composite sample of approximately 40 specimens and chips from Yellowknife sediments.

TABLE 19

GOLD-QUARTZ DEPOSITS IN YELLOWKNIFE GROUP SEDIMENTS

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}(‰)$
62	Composite of sp, gn and py.	Ptarmigan mine.	+0.4
63	Sp.	Ptarmigan mine.	+3.8
60	Py in vug.	Ptarmigan mine.	+2.5
61	Py in seam in quartz.	Ptarmigan mine.	+2.4
98	Gn.	In veins north of Ptarmigan mine.	+1.3
99	Sp.	In veins north of Ptarmigan mine.	+2.2
97	Sp.	Tin Can claim, Prosperous Lake.	+2.0
111	Py.	Walsh Lake.	+2.3
94	Asp and minor py in quartz vein.	Burwash mine.	+4.0
	Average		+2.3
	Weighted average greywacke to slate[1]		+1.8

[1]See Table 18

TABLE 20

PROFILE ACROSS BURWASH VEIN

SAMPLE	DESCRIPTION	LOCATION	$\delta S^{32}/S^{34}(‰)$
96	Py in greywacke.*	Burwash area, relatively unmetamorphosed zone.	+1.6
95	Py and asp in wall-rock alteration zone adjacent to quartz vein.	Burwash mine.	+2.9
94	Asp and minor py in quartz vein.	Burwash mine.	+4.0

TABLE 21

REPRODUCIBILITY OF INSTRUMENTAL ANALYSES

A. Sulfide sample No. 94

Substandard No.	$\delta S^{34}/S^{32}(‰)$	Date Analysed
27	+3.8	20-3-56
27	+4.0	21-3-56
27	+4.0	22-3-56
27	+4.2	23-3-56
27	+4.0	9-4-56
27	+4.2	16-4-56
27	+4.2	16-5-56
27	+4.0	25-5-56
196	+4.0	28-6-56
	$+4.0 \pm 0.14$**	

B. Sulfide sample No. 109

27	+1.8	6-4-56
27	+1.8	24-4-56
27	+1.8	25-4-56
27	+1.8	16-5-56
196	+1.8	12-7-56
196	+1.8	13-7-56
196	+2.0	18-7-56
196	+2.0	19-7-56
196	+2.0	22-8-56
196	+2.0	5-9-56
196	+2.2	10-9-56
196	+2.0	10-9-56
579	+2.0	10-9-56
	+1.8	3-4-58
	$+1.9 \pm 0.12$**	

** Standard deviation

bacteria are active, producing methane and hydrogen sulfide. In view of this, it seems probable that the heavy sulfates in the underground waters are due to the oxidation, in part bacterial, of sulfides in the shear zones and country rocks.

SULFUR ISOTOPE DISTRIBUTION IN YELLOWKNIFE GROUP SEDIMENTS

Country Rocks

Sulfur isotope ratios determined for sulfides from composite samples of the Yellowknife sediments are given in Table 18. All the sulfides in this suite of rocks contain more S^{34} than found in meteoritic troilite, and the ratios are similar to those determined for the sulfides in the amphibolites of the Greenstone belt. A notable feature is that the arkose, greywacke, and quartzite (No. 96) with a low sulfur and carbon content, contains less S^{34} than the graphitic slate and argillite composite (No. 92), which has a relatively high sulfur and carbon content. This is analogous to the relationship found between the siliceous and graphitic tuffs of the greenstone belt.

Since the ratio of greywacke to slate in the field is approximately ten to one this ratio has been used in the calculation of the weighted average ($+1.8‰$) for the sedimentary terrain. This average will be used for comparison with the isotopic values determined for sulfides in the gold-quartz lenses in these rocks.

Deposits

The isotopic values for nine samples from veins in the sedimentary area are given in Table 19. Since all mines are now inactive, no systematic collection was possible, and specimens were selected from mine dumps and surface exposures.

Although there is considerable variation from vein to vein, the isotopic values are similar to those found in the greenstone belt. All samples analyzed contain more S^{34} than found in meteoritic troilite. In addition, the average value of the ore samples is heavier than the weighted average of the greywacke and slate of the country rock.

In a single instance, at the Burwash mine, it was possible to sample systematically across the country rock and alteration zone associated with the vein. The isotopic results, given in Table 20, show that there is an enrichment in S^{34} in the sulfides as one proceeds from the country rock, through the alteration zone, to the ore, with the heaviest values localized in the ore. This distribution is identical to the distribution observed in the alteration zones associated with the orebodies in the shear zones of the greenstone belt.

SUMMARY

This investigation has revealed the following:

1. Sulfides in the western granodiorite contain more S^{34} than the sulfides in any of the other major rock units.

2. The sulfides in the quartz-feldspar porphyries are also relatively enriched in S^{34}, having isotope ratios similar to those of the sulfides in the granodiorite.

3. Sulfides in the metamorphic facies of the greenstone belt are depleted in S^{34} with respect to the sulfides of the western granodiorite. The depletion increases with distance east of the granodiorite-greenstone contact.

4. Tuffaceous rocks, high in carbon and sulfur, contain sulfides enriched in S^{34}, whereas siliceous tuffs, low in carbon and sulfur, contain sulfides depleted in the heavier sulfur isotope. Some of the lightest sulfur ratios were found in the sulfides of the siliceous tuffs.

5. Early pre-ore quartz lenses contain sulfides enriched in S^{32} compared with sulfides in their enclosing country rocks.

6. In all shear zone systems, the sulfide ore is enriched in S^{34} with respect to the sulfides in the neighboring host rocks.

7. No systematic relationship was observed between the isotopic ratio of the sulfides and depth in the mines.

8. The average values obtained for a series of profiles taken across the major alteration haloes fall in a regular progression from the host rocks through the alteration halo to the ore zone, with the heavier sulfur concentrated in the ore.

9. Sulfosalts, stibnite, and galena, which are paragenetically later than pyrite and arsenopyrite in all orebodies, are enriched in S^{32} with respect to associated pyrite and arsenopyrite.

10. Sulfides in post-ore quartz-carbonate lenses contain more S^{32} than the associated sulfide ores.

11. The sulfide minerals adjacent to post-ore diabase dikes have been markedly depleted in S^{32} with respect to sulfides remote from the dike.

12. The isotopic abundance ratios for sulfides in late faults and fractures vary over the whole range defined by this investigation.

13. All of the sulfate samples studied contain more S^{34} than found in sulfides of the region.

14. Sulfides in the Yellowknife sediments have isotopic ratios similar to those found in the amphibolites of the greenstone belt.

15. Sulfides in greywacke, arkose, and quartzites, with a low sulfur and carbon content, contain less S^{34} than sulfides in graphitic slates and argillites, which contain relatively more sulfur and carbon. In this respect the isotopic distribution resembles that found in siliceous and graphitic tuffs of the greenstone belt.

16. Sulfides from all veins in the Yellowknife sediments contain more S^{34} than meteoritic troilite, and the average value of nine ore samples is heavier than the weighted average of sulfides in the greywacke and slate.

17. A profile across the Burwash vein exhibits the same phenomenon observed in the alteration haloes associated with the orebodies of the greenstone belt.

DISCUSSION

It is assumed that the sulfides of the region originally contained the sulfur isotopes in the same proportions as found in meteoritic troilite [2] and that

[2] This postulate seems justified since the Yellowknife sediments probably represent the initial reworking of crustal material and the greenstones (lavas) were derived from a deep-seated primordial source.

the observed distribution has resulted from the subsequent influence of temperature, pressure, and chemical gradients.

The greatest enrichment of the heavier isotope has taken place in those bodies of rock that have been subjected to the highest temperature, namely the western granodiorite, the high-grade metamorphic facies, the porphyritic bodies, and the sulfide ore adjacent to the diabase dikes.

In the western granodiorite the enrichment in S^{34} has resulted in the formation of sulfides with an isotopic ratio of + 5.0‰ heavier than meteoritic troilite. If this body of rock or its antecedent originally contained sulfur with a meteoritic isotope ratio, what has become of the lighter sulfur isotopes? There would appear to be two possible answers to this question: 1) the lighter sulfur isotope migrated into the greenstone rocks which are now found to contain more S^{32} than the western granodiorite; or 2) the lighter species has moved out of the granodiorite and has escaped, i.e. the granodiorite has been out-gassed.

If the sulfur had simply migrated from the granodiorite into the greenstone rocks two features should be observed: a) the distribution should be a smooth function across the granodiorite-greenstone contact, and b) the final overall distribution of the region should be more or less equally spaced on either side of the meteoritic base level. Neither of these distributions has been found. There is a significant break in the distribution function at the granodiorite-greenstone contact, + 5.0‰ to + 1.9‰, which is analogous to a break in the geochemical profiles reported by Boyle (4). In addition it has been shown in Figure 2 that the isotopic distribution is not equally spaced about the meteoritic level and that the overall average is heavier than meteoritic. In fact, only six samples with negative values have been found in a study embracing 140 analyses.

It is of course possible that the primary postulate is in error and that the original distribution was heavier than meteoritic, in which case, the specimens now yielding positive values in the range + 1.0‰ to + 4.0‰ may contain the lighter isotopes that originated in the granodiorite. However, the fact remains that the distribution is not continuous across the contact as would be expected if the lighter isotope had migrated from the granodiorite to its present location in the greenstone rocks. The most appealing explanation is that both the granodiorite and greenstone rocks have been out-gassed during granitization and metamorphism. In this respect, it should be noted that the rocks of the amphibolite facies adjacent to the granodiorite-greenstone contact have lost a greater percentage of the lighter sulfur isotope than those in the cooler facies, indicating that the thermal history of the rocks has been responsible for the observed isotopic distribution.

Further evidence in support of the conclusion that thermal gradients may be responsible for the preferential diffusion of the lighter isotope away from the higher temperature zones is to be found in a consideration of the sulfides adjacent to the diabase dikes. In both of the cases studied the lighter isotope has migrated away from the zone adjacent to the dike thereby causing the sulfides in the hotter zone to become markedly enriched in the heavier sulfur isotope.

Pressure gradients have also been responsible for the modification of the isotopic distribution. Sulfides in isolated lenses filling tension fractures in the epidote-amphibolite facies always contain more S^{32} than sulfides in the enclosing country rocks, indicating that the lighter isotope has been more mobile. Identical relationships have been observed in post-ore quartz-carbonate lenses.

During the formation of the large gold-quartz orebodies, pronounced chemical and pressure gradients existed, resulting in the formation of marked alteration zones about the gold-quartz lenses. From this investigation it is evident that the heavier sulfur isotope has been retained to a greater extent in the zones that have undergone extensive chemical change, and that large quantities of S^{32} diffused up the shear zone systems to the surface, thereby producing the observed sulfur isotope profiles from the country rock to the ore. As shown in Figure 4, the average values for the sulfide ore bear a relationship to the country rock in which the shear zones occur, suggesting that the sulfur now found in the orebodies originated in the associated country rocks. The magnitude of the sulfur isotopic enrichment has been found to be approximately the same in each of the transecting systems investigated.

The sedimentary area east of Yellowknife Bay was not studied in comparable detail, but the results available show that the isotope ratios have been modified in a similar manner and to a comparable degree. The orebodies, once again, contain sulfides enriched in S^{34} with respect to the greywackes and slates in which they occur. A single profile across the country rock, and alteration zone at the Burwash mine exhibits the same gradual enrichment in S^{34} as one approaches the ore. It has also been noted that the slates, which contain more graphite, contain sulfides with more S^{34} than the greywackes in which the graphite content is extremely low. This relationship is analogous to that observed for the graphitic and siliceous tuffs of the greenstone belt.

CONCLUSIONS

1. The original sulfur isotopic distribution of the region (assumed to be meteoritic) has been modified by the temperature gradient existing during granitization and metamorphism. Rock units that have had high thermal histories (western granodiorite, porphyries, diabase dikes) all contain, or are associated with, sulfides that have been enriched in S^{34}.

2. Sulfides in dilatant zones and post-ore tension fractures contain more S^{32} than sulfides in their enclosing rocks, indicating that pressure gradients have been responsible for the differential migration of the lighter sulfur isotope.

3. Under conditions of intense chemical activity, existing during the formation of the large gold-quartz orebodies and their associated alteration haloes, the heavier sulfur isotope was preferentially retained in the regions of greatest activity (the ore zones) creating the sulfur isotopic profiles observed between the country rock and ore zones.

4. The enrichment of the S^{34} has been found to be of the same order of magnitude in each of the major shear zone systems, indicating that each

system developed from the base level found in the associated metamorphic facies, and that the sulfides now found in the ore zones probably originated in the associated country rocks.

5. Graphitic tuffs contain sulfides enriched in S^{34} compared to the carbon-free siliceous types. A similar, though less marked relationship exists between slates and greywackes in the Yellowknife sediments. It is suggested that life processes may have been responsible for the enrichment of S^{34} in the graphitic rocks.

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OTTAWA, ONTARIO,
May 6, 1960

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APPENDIX

Experimental Procedures

Conversion of Sulfide Minerals to Sulfur Dioxide.—The apparatus, illustrated in Figure 7, was employed for the conversion of sulfide samples to

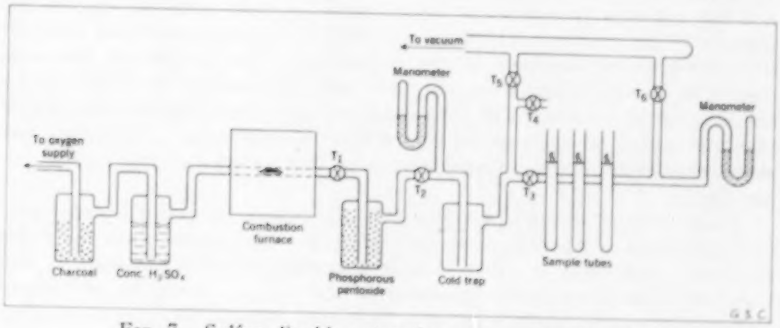

FIG. 7. Sulfur dioxide extraction and purification line.

sulfur dioxide for mass spectrometric analysis. The quartz combustion tube, generally used by other workers, was replaced by a high temperature Leco [3] furnace. This modification was incorporated to permit combustion of sulfides above the dissociation temperature of SO_3, thereby eliminating possible fractionation of the sulfur isotopes between the SO_2 and SO_3 molecular species. The sample (approximately 100 mg of pyrite or equivalent weight of other sulfide mineral) was mixed with an equal weight of pure tin pellets to accelerate the combustion, and placed in a sulfur-free combustion boat. The oxygen used for all conversions was drawn from the same cylinder, thereby ensuring a constant oxygen isotope distribution.

The oxygen, after purification by passage through an activated charcoal trap, maintained at dry ice temperature, and concentrated H_2SO_4, was allowed to flow through the combustion tube and extraction line for some minutes

[3] Leco #2600—Laboratory Equipment Corporation, St. Joseph, Michigan.

before the sample was placed in the furnace. During this period stopcocks T_1, T_2 and T_4 were open; T_3, T_5 and T_6 were closed. Stopcock T_1 was then closed, the sample boat was placed in the furnace, and a cobalt glass combustion tube window was inserted into the end of the tube to permit observation of the reaction. As gases evolved the oxygen pressure was adjusted to prevent the flow of H_2SO_4 into the charcoal trap. After a combustion period of three to four minutes the gases were condensed in the cold trap maintained at the temperature of liquid oxygen, excess oxygen being allowed to escape via T_4. When all of the combustion products were swept from the furnace, T_1 and T_4 were closed, T_5 was opened and the residual gas was transferred from the P_2O_5 trap to the cold trap. T_2 and T_5 were then closed and the liquid oxygen on the cold trap was replaced by a mixture of acetone and dry ice. At this temperature CO_2 and other volatile impurities were released, and the resulting pressure was indicated on the manometer. The volatile gases were then exhausted via T_5. The purified SO_2 was then transferred, via T_2, to an evacuated sample tube maintained at the temperature of liquid nitrogen. After all of the gas was transferred, T_3 was closed, the liquid nitrogen was removed from the sample tube and the gas was permitted to expand into the line. An estimate of the quantity of gas produced and hence the yield of the combustion was obtained from the pressure indicated on the manometer. The combustion was considered to be satisfactory when the yield indicated conversion of 95% of the sulfur to sulfur dioxide. The gas sample was then condensed into the sample tube and sealed off for transfer to the mass spectrometer. Experience has shown that eight to ten sulfide conversions may be satisfactorily carried out per day.

Conversion of Sulfates to Sulfur Dioxide.—Since the sulfur isotopes may be fractionated in laboratory chemical processes our original plans called for the direct conversion of sulfate sample materials to sulfur dioxide. It was hoped that the temperature produced in the furnace would be sufficiently high to dissociate completely the SO_4 molecules and that the oxygen supplied for the combustion would completely replace the oxygen liberated. In practice, however, we found that replicate combustions of the same sulfate sample did not yield reproducible sulfur isotope ratios. Preliminary conversion of sulfate to silver sulfide or cadmium sulfide was therefore carried out employing the method reported by Rafter (19).

Instrumental Analyses.—The isotopic analyses are reported as permil deviations from a sample of meteoritic troilite [4] which has been assigned a value of 0.0‰. The permil values are calculated from the relationship:

$$\delta S^{34}‰ = \frac{S^{34}/S^{32}\ (\text{Standard}) - S^{34}/S^{32}\ (\text{Sample})}{S^{34}/S^{32}\ (\text{Standard})} \times 1000$$

Positive values indicate an excess of S^{34} with respect to the meteoritic standard while samples enriched in S^{32} have negative values.

[4] Troilite from a sample of "Merceditas," a medium octrahedrite, found at Chanaral, Atacama, Chile.

Simultaneous collection techniques (27) were employed for all sulfur isotope analyses. A two-litre bulb containing purified SO_2 produced from a large pyrite sample, arbitrarily chosen as a substandard, was permanently attached to one of the two sample handling lines of the mass spectrometer. A small volume of this gas was admitted to the instrument for each group of analyses, the residue being pumped away when the analyses were completed. One of the samples previously analyzed was re-analyzed with each new group, thereby providing a day to day check on the composition of the substandard and on the instrumental operation.

The results of replicate analyses carried out on two samples over a period of some months are given in Table 21. It will be noted that the standard deviation of the average of the replicate analyses is less than 0.2‰.

The isotopic results given in Table 21 also reflect the reproducibility of the conversion of sulfide minerals to sulfur dioxide. Substandard samples numbers 27, 196 and 579 represent SO_2 conversions from the same pyrite sample over a period of two years. Variations for the substandards are of the same order of magnitude as found for replicate instrumental analyses from day to day.

Economic Geology
Vol. 55, 1960, pp. 1622–1630

DIFFERENCES BETWEEN BARREN AND PRODUCTIVE INTRUSIVE PORPHYRY[1]

BRONSON STRINGHAM

ABSTRACT

It has been statistically shown that a great majority of the larger Cretaceous and younger hydrothermal ore deposits of Au, Ag, Cu, Pb, Zn, Mo, Hg, and U in the Basin and Range Province are associated with intermediate to acidic intrusive aphanitic or porphyritic rocks of near similar age. Recent work indicates that, except for the Pacific Coast Ranges and the Mother Lode area, similar ore-porphyry relationships apply to deposits over the entire western U. S. However, many intrusive porphyries exist that have little or no associated hydrothermal deposits. Some intrusive porphyries, therefore, seem to be genetically related to ore deposits while others are not. These then may conveniently be classified into 2 categories as barren and productive.

To aid further the ore finder, an attempt is made here to offer criteria that will serve to distinguish barren from productive porphyries.

Among the many suggestive distinctions the following seem to be of most importance. Productive acid porphyry bodies generally are of considerable size and seem to cross cut enclosing rock structures with very little or no disturbance due to intrusive action. On the other hand barren porphyries may be of various sizes but on the whole have a tendency to either be concordant with wall rock structures or, where cross cutting relations exist, show obvious intrusive structural effects such as brecciation, folding, or up arching. Other criteria are listed in order of importance in Table II of the paper.

INTRODUCTION

THE close areal relationship of Cretaceous or later intrusive porphyries to larger hydrothermal deposits of Pb, Zn, Au, Ag, Cu, Mo, Hg, and U of similar age in the Basin and Range Province, was statistically shown in a recent paper (17). During the past year this study has been expanded to cover all of the larger hydrothermal deposits of similar nature occurring in the entire western United States. The results of this work was presented before the A. I. M. E. at Moab, Utah in May, 1959. The statistics of the porphyry-ore relationships throughout the West as a whole turned out to be so similar to the first study of the Basin and Range Province that an independent report is not now contemplated.

The term hydrothermal is used here in the sense of magmatic hydrothermal of Jensen (8), thus the sandstone type uranium deposits of the Colorado Plateau and Wyoming have been excluded since considerable controversy exists regarding their origin. This relationship then leads to the conclusion that when exploring for similar types of hydrothermal deposits of the metals

[1] Assistance has been received from the Kennecott Research Fund and the University Research Fund, University of Utah.

considered one may feel reasonably sure that if an intrusive porphyry of considerable size is not present he may be facing much greater risk of finding an ore body than if a porphyry were present.

Since there are many intrusive porphyritic rocks that do not seem to be associated with hydrothermal deposits, it is believed that some distinct value can come from the recognition of intrusive porphyry that might be barren, as well as the intrusive porphyry that might be productive. This paper deals with that problem.

DEFINITIONS OF TEXTURES

Due to diverse spheres of training, there is often disagreement among geologists as to the strict definition of certain rock textural terms, and since texture is of ultimate significance here, the definitions employed are given.

It is believed that nature herself has properly separated igneous rock textures into two distinct categories and in recognition of this, an old, well-established terminology is used (10). The granitoid or granitic texture, characteristic of intrusive rocks exclusively, can be described as one where the rock is non-foliated, but all minerals except accessories are visible to the unaided eye, pegmatites excepted, however. This term also includes granitoid rock with large phenocrysts commonly referred to as porphyritic granite, porphyritic diorite, etc.

The other terms are characteristic of extrusive and intrusive bodies. These include glassy as well as aphanitic, wherein the rock appears to be crystalline but minerals are too small to be readily perceived by the unaided eye. This texture includes such rocks as aphanite, felsite, and even aplite as used by some authors. The term porphyritic as used here will refer to rocks having an aphanitic groundmass with visible phenocrysts such as rhyolite porphyry. It is unfortunate that the terms granite porphyry, diorite porphyry, etc., are also in general use for rocks with an aphanitic groundmass where phenocrysts predominate. It is hoped that in the future these latter terms may be deleted entirely from petrological nomenclature so that the confusion that exists between the terms porphyritic granite and granite porphyry, for example, will not be perpetuated.

MINING DISTRICTS STUDIED

A total of 207 mining districts in the western United States having produced values over $3,000,000 in Pb, Zn, Au, Ag, Cu, Mo, Hg, U and W were reviewed for the purpose of making evaluations incident to intrusive porphyries versus other types of related intrusive rocks. It is hoped that no deserving district has been missed, and if such is the case, it is an oversight. Of this number, 127 have been observed first hand by the author. The other 80 have been studied through the literature. A listing of the references reviewed is not included because it would be much too extensive for this paper. The map shown in Figure 1 of the western United States contains all of the 207 localities considered. To show a measure of size and perhaps importance as was done previously (17), these districts are

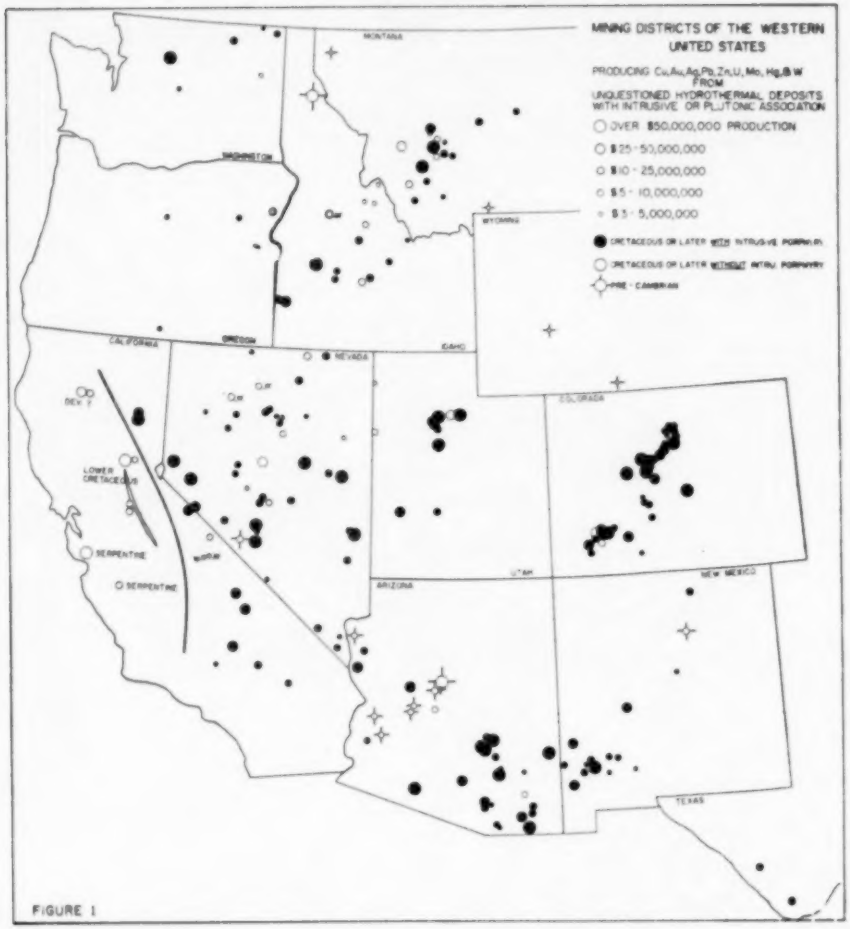

FIGURE 1

designated in terms of their most recently known production figures into five categories as $3–5,000,000, $5–10,000,000, $10–25,000,000, $25–50,000,000, and over $50,000,000 in value. It will be noted that 15 of these deposits are considered to be Precambrian in age, and that five of them, none of which contain intrusive porphyry, are prominant tungsten producers. The deposits of the west slope of the Sierra Nevada and the West Coast ranges seem to be of a different nature than those under consideration. The Shasta districts may be Devonian in age and the Mother Lode, Copperopolis, Campo Seco, Grass Valley, and Allegheny are probably Lower Cretaceous; the two mercury deposits New Almaden and New Idria are associated principally with serpen-

tine and basic rocks. It is presumed practical to consider only the Late Cretaceous and Tertiary deposits of the west in this evaluation for the reason that older deposits may be somewhat changed from their original condition through metamorphism and the younger ones present the best opportunity to observe deposits containing rocks and minerals in what might be the most original or unchanged condition and are therefore more reliable for interpretation. If we exclude then those deposits occurring in the Sierra Nevada and the West Coast, the 15 Precambrian and the five tungsten producing districts, there are left 179 districts of Late Cretaceous or Tertiary age. In 25 of these districts there is no exposed intrusive porphyry of significant size. In accumulating criteria characteristic of a productive porphyry, then, the remaining 153 districts have been critically reviewed and evaluated for this purpose.

STRUCTURAL CLASSIFICATION OF INTRUSIVE PORPHYRIES

The most significant feature that distinguishes productive from barren intrusive porphyries has proved to be one involving the structural attitude of the country rock surrounding the porphyry. For this reason, they have been classified here into three types: (1) forceful, (2) passive, and (3) permissive.

The forceful type of intrusive is one that obviously has been injected by magmatic pressure and has pushed aside rocks to make room for itself. These types are exemplified by laccoliths, intrusive breccia, sills, dilation dikes, and various types of concordant features. These may be specifically illustrated by many well-known examples from the literature describing such geologic features as the La Plata Mountains (*2*), Henry Mountains (*7*), or any of those numerous reports describing the laccoliths and related intrusives of the Colorado Plateau, Montana, or Wyoming. Also included in this type are volcanic breccias that are presumed to have been once a volcanic vent such as that of Cripple Creek (11) or at Spanish Peaks (6). These distinctive structural types would be fairly judged by any impartial observer to have been implaced under magmatic pressure or forceful conditions.

The passive type intrusion is one that cross-cuts wall rock formations apparently without injection effects or structural features sympathetic to forceful implacement. The room problem here becomes one of importance. Examples may be seen in reports on Bingham (16), Park City (1), Ely (15), Morenci (12), and many others. The cross-cutting passive intrusives may have fairly large dilation dikes shooting off from the main body and these may have forceful intrusive characteristics so that in reality both passive and small scale forceful conditions may be observed in a single district.

The permissive type has an unusual structural relationship in that an observer may use the evidence he finds for either forceful intrusion or passive intrusion depending upon his viewpoint. Permissive intrusives have been noted in several places in the Basin and Range where country rock dips away from the intrusive on all or nearly all sides such as at Whitehorse, Nevada (personal observation) or Newfoundland Range, Utah (14), and Tombstone,

Arizona (5). However, in these cases there is also shown to be a marked cross-cutting effect by the intrusive since it has implaced the country rock along the borders in a quiet or passive manner regardless of the upturned structure. Permissive, therefore, could mean that the structure was present before intrusion, or it could mean that intrusion was responsible for the structure now existing.

CLASSIFICATION OF PRODUCTIVE PORPHYRIES

The 153 productive districts of the western United States where larger masses of intrusive porphyry occur are grouped in Table I according to the

TABLE 1

153 OF THE 207 MINING DISTRICTS OF THE WESTERN UNITED STATES CONTAINING INTRUSIONS OF APHANITIC ROCKS

Over $50,000,000	$25–50,000,000	$10–25,000,000	$5–10,000,000	$3–5,000,000
Intrusive Porphyry *Passive*, Larger Masses				
Arizona	*Arizona*	*Arizona*	*Arizona*	*Arizona*
Ajo	Bagdad	Castle Dome	Patagonia	Harshaw
Bisbee	Oatman	Chloride	*California*	Helvitia
Miami—Globe	Silver Bell	Christmas	Ludlow	Mammoth
Morenci	Twin Buttes	Esperanza	*Colorado*	*Colorado*
Ray	*California*	*California*	Bonanza	Caribou
San Manuel	Cerro Gordo	Calico	Chalk Creek	Freeland—Lamartine
California	Darwin	*Colorado*	Empire	Lawson—Dumot
Walker	Engel	Breckenridge	Jamestown	Summitville
Colorado	Randsburg	Kokomo	Lake City	Tincup
Aspen	*Colorado*	Monarch	Ophir	*Montana*
Eureka	Creede	Red Mountain	Tomichi	Clancy
Central City	Georgetown—Silver Plume	*Idaho*	Ward	Rimini
Climax	Montezuma	De Lamar	*Idaho*	Virginia City
Idaho	*Idaho*	Yankee Creek	Atlanta	*Nevada*
Boise Basin	Silver City	*Montana*	Mackay	Bullfrog
Montana	*Montana*	Elkhorn	Rocky Bar	Bullion
Butte	Marysville	Neihart	*Montana*	Divide
Wickes	*Nevada*	*Nevada*	Dillon	Eldorado
Nevada	Aurora	Candelaria	Pony	National
Ely	*New Mexico*	Copper Canyon	Radersburg	Seven Troughs
Eureka	Lordsburg	Delamar	*Nevada*	Tenabo
Goldfield	Magdalena	Goodsprings	Copper Basin	*New Mexico*
Tonopah	*Utah*	Hamilton	Fairview	Chloride Flat
Virginia City	Ophir	Manhattan	Rochester	Cooks Peak
Yerington	San Francisco	Round Mountain	Search Light	White Oaks
Utah	Stockton	Tuscarora	Unionville	*Washington*
Bingham		Tybo	Wonder	Northport
Park City		*New Mexico*	*New Mexico*	Wenatchee
Tintic		Mogollon	Hillsboro	
Washington		Questa	Kingston	
Holden		Pinos Altos	Steeple Rock	
		Tyrone	*Washington*	
		Utah	Metaline	
		Marysvale		
		Mercur		
		Washington		
		Republic		

Total 121 Districts 79%

TABLE 1—*Continued*

Over $50,000,000	$25–50,000,000	$10–25,000,000	$5–10,000,000	$3–5,000,000
Intrusive Porphyry Present as *Dikes* Only				
Colorado Gilman *Nevada* Pioche	*California* Bodie	*Arizona* Pierce *Colorado* Boulder Co Gold Hill *Idaho* East Wood River *Nevada* Jarbridge	*Arizona* Kofa *Colorado* Gladstone *Nevada* Bristol Gold Acres	*Idaho* Texas Creek (Gilmore) *Oregon* Cracker Creek
14 Districts 9%				
Intrusive Porphyry *Permissive* (Two Interpretations)				
Arizona Superior *Colorado* Leadville *New Mexico* Central	*Arizona* Tombstone	*Arizona* Courtland— Gleeson		*Arizona* Aravaipa *California* Mohave
7 Districts 5%				
Intrusive Porphyry *Forceful*				
Colorado Cripple Creek	*Colorado* Alma Ouray Rico	*Texas* Shafter Turlingua	*Colorado* La Plata *Montana* Kendall	*Nevada* Lewis *Oregon* Horse Heaven Lakeview
11 Districts 7%				

above structural classifications. Table I shows 121 districts or 79 percent of the whole, all of which exhibit a good measure of the passive type intrusion. It is true that some of these districts having smaller porphyry bodies, may show some of the characteristics of the forceful type. Districts are grouped according to their location by state and production for convenience in review and to aid the reader in finding districts he regards as important. Table I also contains districts classified as permissive, forceful, and a category where small dikes only are present as an associated intrusive. Examples of the latter do not have charateristics that place them firmly in any of the other groups. The district containing dikes only, number 14 or 9 percent of the whole. Seven districts, or 5 percent are judged to be in the permissive classification, whereas 11 districts or 7 percent show conditions of an obvious forceful type. It would seem from these statistics that the passive intrusion, being much more commonly associated with known mineralization than the

TABLE 2

INTRUSIVE PORPHYRIES
CRITERIA LISTED IN ORDER OF IMPORTANCE

Barren	Productive
1. Classification—forceful. Structure—concordant, sheets, sills, laccoliths, bysmaliths, intrusive breccia, etc.	1. Classification—passive. Structure—cross cutting.
2. Strong flowage features.	2. Weak flowage features (except in smaller bodies, dikes, etc.).
3. Prominant cooling features. Chilled borders. Great variations in grain size, directly related to borders and size of intrusion.	3. Cooling features very weak. Little variation in grain size. Smaller bodies tend to have fewer phenocrysts.
4. May have varied composition. Particularly of basic & alkalic rocks. Where stratification could be prominant.	4. Uniform composition. Rock types restricted to alaskite porphyry through diorite porphyry or rhyolite through andesite.
5. May or may not have glassy groundmass.	5. Glassy groundmass essentially absent.
6. Borders toward related granitoid rock may be gradational.	6. Borders sharp, even toward related granitoid rock.
7. Little contact action on wall rocks.	7. Much contact action where wall rock composition is unlike intrusive (rhyolite—limestone).
8. Usually not altered (propylitization and weathering excepted).	8. May or may not be altered but strong alteration is definitely encouraging.
9. Phenocrysts not likely to be scalloped by groundmass.	9. Phenocrysts may be scalloped by groundmass.

other type, is therefore statistically much more likely to be associated with an ore body in an unknown or unproven district.

BARREN PORPHYRIES CONSIDERED

The consideration of any barren porphyry has some ambiguous conditions connected with it. For instance, it is almost impossible to prove that a porphyry *is* a barren one since the lack of discovered mineralization is not proof that there is not or never was strong mineralization in the area. However, quite a number of porphyries, so far proven to be barren, have been reviewed and observed. A common characteristic of most of these intrusives is the fact that they appear to have a forceful structural environment. In addition to the laccoliths of Montana, Wyoming, and Colorado Plateau noted earlier, several at present barren intrusive porphyries have been observed in Nevada and seem to have similar characteristics such as Lone Mountain (13), and Swalls Mountain (personal observation), both northwest of Elko, and the Cortez Mountain intrusive porphyry (personal observation), located about ten miles north of the Cortez district.

A few others, chiefly intrusive porphyries in Nevada personally visited, do not plainly show structural characteristics of forceful intrusion but other criteria indicate they fall into the barren category. These include a porphyry

described by Knopf (9), in the South Yerington district and the aplites and intrusive porphyries that Ferguson (4) described in the Mina and Round Mountain (3) quadrangles and several others which have been personally observed.

Satisfactory data on the barren porphyry is admittedly far from complete. This is partly due to the fact that areas where they occur are uninteresting economically and as a result comparatively little detailed published information is available except in localities of academic interest such as the laccolith groups. As a consequence of this, the evidences or criteria developed in the present study on barren porphyries may be considered weak in comparison with the productive porphyries. The attempt, however, to evaluate barren porphyry has been made regardless of the paucity of data, and it is hoped that some good will come of the effort.

DIFFERENCES BETWEEN BARREN AND PRODUCTIVE INTRUSIVE PORPHYRY

In Table II are listed the criteria that have been assembled as a result of the writer's studies, distinguishing barren from productive intrusive porphyries. It has already been shown that the most critical feature is one of structure and this is, therefore, listed first. Other criteria are listed in what is believed to be their order of importance. It should be understood by any geologist that criteria such as listed here can only be valid where keen observation and mature judgment has been used in gathering the facts and the interpreted conditions present in any area under investigation. These criteria are also not rigid and are subject to some flexibility. An experienced ore finder would use the criteria together with his best professional judgment. Conditions found in an intrusive porphyry may not all fit into the barren or the productive category. In this case considerable caution should be exercised in final evaluation. However, it is believed that if one should find a set of conditions applying wholely or in large part to the criteria for barren porphyry, it is thought he should likely leave the project alone on the grounds that a great deal of added risk is involved. On the other hand, if he finds an intrusive porphyry with strong productive characteristics, he should feel justified in extending his explorations further until he is convinced that ore does not exist within economic reach.

THEORY

Most of the criteria listed here are based upon observed conditions, but one of the difficulties as pointed out above of establishing reliable data on the so-called barren porphyry is that it is not absolutely known to be barren. It is realized that the criteria such as that given here possibly would be better understood if theory was presented along with them. In order to expand the criteria, some theoretical thoughts were used in the establishment of some of the criteria and it is sorely tempting to offer these theories for consideration here. However, theory is not intended to be part of this presentation and the author prefers to defer presentation of theory to a subsequent date.

ACKNOWLEDGMENTS

This study would not have been possible without the aid of the Kennecott Research Fund and the University Research Fund at the University of Utah, and thanks is here offered to the administrators of those funds.

Armand J. Eardley has taken special interest in this work and to him is offered appreciation. A small geological discussion group of Salt Lake City offered very valuable advice during the preparation of the paper and most grateful thanks is tendered to them.

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SALT LAKE CITY, UTAH,
April 2, 1960

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Economic Geology
Vol. 55, 1960, pp. 1631–1652

THE Fe-As-S SYSTEM: PHASE RELATIONS AND APPLICATIONS[1]

LLOYD A. CLARK

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PROBLEMS OF ARSENOPYRITE SYNTHESIS

As shown in Table 15, numerous attempts were made to synthesize arsenopyrite, both in sealed, evacuated silica tubes and in gold tubes under approximately 2,070 bars confining pressure. Various starting materials were combined to give bulk compositions equivalent to FeAsS and to many other bulk compositions as well. The products, with one exception, contained small percentages of pyrrhotite. Even with bulk compositions in the arsenopyrite-arsenic-liquid-vapor region at 600° C, 2 to 3 percent of metastable pyrrhotite persisted as cores within arsenopyrite grains after heating for 1 month. It was possible, however, to open such a run (for example, the runs listed 8th and 9th in Table 15), grind its contents under acetone,[40] and then re-heat. After the second 2- to 3-week heating period at 600° to 650°

[1] Part of a dissertation presented to the faculty of McGill University in candidacy for the degree of Doctor of Philosophy.

[40] The losses incurred had no effect on the results as long as the bulk composition of the charge remained within the same univariant assemblage.

C, the arsenopyrite was almost free (perhaps 0.1 percent remained) from metastable pyrrhotite cores. Near the end of the heating period, the tube was moved in the furnace so as to give a gradient of about 5° C along its length. In a few hours the coexisting arsenic and liquid collected in the cool end of the tube where a small free space had been left. Thus, they were easily separated when the tube was quenched and opened.

In the run listed 11th in Table 15, $FeAs_2$ was combined with an arsenic-sulfur glass to give a bulk composition in the arsenopyrite-arsenic-liquid-vapor region at the temperature of the run. (The sulfur-arsenic glass was of the

TABLE 15

Attempts to Produce a Pure Arsenopyrite Phase in Silica Tubes

Bulk composition, weight percent			Starting reagents	T, °C	Time, days	Phases in product. Not necessarily all stable.
Fe	As	S				
*34.3	46.0	19.7	Fe, As, S	600	4	Asp + Po + L + V
*34.3	46.0	19.7	FeS, As	550	8	Asp + Po + L + V
*34.3	46.0	19.7	FeAs, S	550	30	Asp + Po + L + V
*34.3	46.0	19.7	FeS_2, $FeAs_2$	550	18	Asp + Po + L + V
35.2	42.5	22.3	FeS_2, $FeAs_2$	600	6	Asp + Po + L + V
33.8	47.7	18.5	FeS_2, $FeAs_2$	600	10	Asp + Po + L + V
33.4	49.3	17.3	FeS_2, $FeAs_2$	600	21	Asp + Po + L + V
23.5	63.0	13.5	$FeAs_2$, S	600	9	Asp + As + Po + L + V
33.0	51.0	16.0	$FeAs_2$, S	600	19	Asp + As + Po + L + V
32.9	51.3	15.8	FeS_2, $FeAs_2$	600	36	Asp + Lo + Po + V
33.4	49.4	17.2	$FeAs_2$, $As_{77}S_{23}$	635	42	Asp + L + V
33.3	46.7	20.0	Fe, AsS	600	59	Asp + Po + L + V
33.0	48.0	19.0	FeS_2, $FeAs_2$, S	600	59	Asp + Po + L + V
			Similar Experiments in Gold Tubes at Approximately 2,070 Bars Confining Pressure			
*34.3	46.0	19.7	FeS_2, $FeAs_2$	590	3	Asp + Po + L
*34.3	46.0	19.7	FeS_2, $FeAs_2$	600	7	Asp + Po + L
33.0	51.0	16.0	FeS_2, $FeAs_2$	600	2	Asp + Lo + Po + As(?)

*These runs have a bulk composition corresponding to the FeAsS formula.

composition saturated with arsenic at 600° C.) In this case, no metastable pyrrhotite formed, and pure arsenopyrite was obtained after a single heating. Temperatures up to about 680° C could be employed, which reduced the heating period to approximately 2 weeks.

STUDIES ON THE COMPOSITION OF SYNTHETIC ARSENOPYRITE

Careful location, at 600° C, of some of the tie-lines in the system, especially those bounding the pyrrhotite-arsenopyrite-vapor divariant region, led to the belief that synthetic arsenopyrite contained more arsenic than was indicated

by the ideal FeAsS formula. The problems of vapor loss and the persistence of pyrrhotite as metastable cores in arsenopyrite grains prevented further investigation of the problem by the usual methods. It was possible to estimate the arsenopyrite composition in one univariant assemblage by the somewhat indirect method described below. Further, it was demonstrated, using X-ray powder diffraction data, that the maximum compositional variation at any given temperature and pressure is very small. Finally, the variation of the arsenopyrite composition as a function of temperature was investigated.

Experimental Determination of Arsenopyrite Composition

The composition of arsenopyrite in coexistence with liquid, arsenic, and vapor is fixed at any given temperature.[41] Using the silica tube-in-tube technique, it was possible to weigh precisely the total arsenopyrite produced in a run. The weight of iron in the original charge was easily calculated from the known compositions of the starting materials; and since, as previously shown, over 99.8 percent of the iron would enter the arsenopyrite, the weight, and weight percent, of iron in the arsenopyrite was obtained. Two preliminary runs gave 33.1 and 34.0 weight percent iron. A later, more precise determination using larger weights of material gave 33.38 weight percent iron for arsenopyrite synthesized at 635° C. The combined weight of sulfur plus arsenic was known by difference, but the ratio between them could not be obtained by this method. The cation-to-total-anion ratio was assumed to be 1 : 2, as in the related structures of marcasite and loellingite (15). The arsenic-to-sulfur ratio, and finally the complete formula, was calculated on this basis. An iron content of 33.38 weight percent gives the formula $Fe_1As_{1.102}S_{0.897}$.[42] This contains 3.4 weight percent more arsenic than the ideal formula FeAsS. (The position of the bulk composition FeAsS is shown at the center of Figures 2 and 3 by a small triangle.)

Using the same data given above, the formula calculation could also have been based on the entirely different assumption that the arsenic-to-sulfur ratio was unity and that iron was deficient in the structure. This would give the formula $Fe_{0.96}AsS$. This assumption is unfounded as is shown by the tie-line locations (Fig. 3) and a chemical analysis.

Chemical Analysis of Synthetic Arsenopyrite

A sample of synthetic arsenopyrite was chemically analyzed as a further check on its composition. These results, shown in Table 16, calculate to $FeAs_{1.160}S_{0.896}$. The material for analysis was synthesized from a bulk composition in the arsenopyrite-arsenic-liquid-vapor region. The starting materials were synthetic $FeAs_2$ and an As-S glass containing 81 weight percent arsenic. These were heated 57 days at 660° C, after which time the arseno-

[41] This is a univariant assemblage where if the temperature is fixed then the total pressure, the partial vapor pressures, and the compositions of all the phases are fixed.

[42] On subsequent pages this formula is written $FeAs_{1.1}S_{0.9}$. This composition lies within the limits of error of the above value, and no difference in composition is implied.

TABLE 16

Chemical Analysis* of Arsenopyrite Synthesized in the Arsenopyrite-Arsenic-Liquid-Vapor Region at 660° C

	Weight percent	Recalculated omitting silica	
		Weight percent	Atomic percent
Fe	32.16	32.57	32.72
As	50.05	50.68	37.97
S	16.54	16.75	29.31
SiO_2	1.05	———	———
	99.80	100.00	100.00
Relative atomic ratio		1 : 1.160 : 0.896	
Relative cation-to-anion ratio		1 : 2.056	

*Analysis by H. B. Wiik and Paavo Vuorinen, Helsinki.

TABLE 17

Variation of the Arsenopyrite 131 Spacing with Different Assemblages at 600° C

Starting materials	T, °C	Time, days	Phases present	d131 Å
FeAs + $As_{50}S_{50}$	600	48	Asp + Lo + As + V	1.6364 ± 0.0003
FeAs + $As_{50}S_{50}$	600	48	Asp + As + L + V	1.6366 ± 0.0003
Fe_2As + $As_{60}S_{40}$	600	151	Asp* + Po + Lo + V	1.6361 ± 0.0003*
Fe_2As + $As_{50}S_{50}$	600	47	Asp + Po + L + V	1.6353 ± 0.0003

*Since the reaction rates in this assemblage are extremely slow, it is uncertain whether or not the composition of the arsenopyrite has reached an equilibrium value.

TABLE 18

Variation of the Arsenopyrite 131 Spacing as a Function of Synthesis Temperature

Starting materials	T, °C	Time, days	d131 Å
(a) Bulk composition lying in the arsenopyrite-pyrrhotite-liquid-vapor region at each temperature			
Fe_2As + $As_{50}S_{50}$	660	48	1.6372 ± 0.0002
" "	630	64	1.6368 ± 0.0003
" "	600	47	1.6353 ± 0.0003
" "	550	84	1.6346 ± 0.0002
" "	500	86	1.6340 ± 0.0003
" "	450	66	1.6330* ± 0.0003
" "	400	86	1.6320* ± 0.0003
(b) Bulk composition lying in the arsenopyrite-loellingite-arsenic-vapor region at each temperature			
$FeAs_2$ + $As_{77}S_{23}$	660	150	1.6379 ± 0.0001
" "	635	42	1.6372 ± 0.0002
FeAs + $As_{50}S_{50}$	600	48	1.6364 ± 0.0003
" "	550	59	1.6358 ± 0.0003
" "	500	59	1.6353 ± 0.0003
" "	450	62	1.6348 ± 0.0003

*The assemblage produced should have contained pyrite rather than pyrrhotite because of the tie-line change Po + L → Py + Asp in effect below 491° ± 12° C (see Fig. 7a). Its absence is unexplained and may render these 131 measurements questionable.

pyrite was separated from the arsenic and liquid by differential heating of the tube. Polished sections of the arsenopyrite showed minor amounts of silica and pyrrhotite as the only impurities. An exhaustive point count, using a method similar to that described by Chayes (21), indicated less than 0.1 percent pyrrhotite. When separated and X-rayed, the silica impurity proved to be cristobalite. The As-S liquid and vapor in the run had transported silica from the tube wall and deposited it throughout the charge as almost spherical, 20 micron grains. The silica came out as "insoluble" in the chemical analysis, and the effect caused by the small amount of pyrrhotite was assumed to be negligible. The analysis was performed by Drs. H. B. Wiik and Paavo Väänänen of Helsinki, who were supplied with approximately 1.75 g of material.

Variation in Arsenopyrite Composition at 600° C

Since it is not possible to grow pure arsenopyrite directly from a charge having the same bulk composition as the arsenopyrite to be produced, the investigation of possible variations in arsenopyrite composition had to be carried out by a less direct means. The *d*-values of arsenopyrites synthesized in the four univariant regions surrounding arsenopyrite vary slightly. Significant differences appear only with careful measurements of some of the high angle, single-index reflections on the diffractometer pattern. Table 17 shows variations in the 131 spacing for arsenopyrites synthesized in the four univariant regions containing this compound at 600° C. In natural arsenopyrite the 202 reflection is the most sensitive to compositional variations. This reflection is sometimes difficult to measure due to poor resolution, and in synthetic arsenopyrite it merges with the $\frac{321}{123}$ compound reflection and cannot be resolved or measured. On the other hand, the 131 reflection, while being less sensitive to compositional variations, is always well resolved, is close to a CaF_2 standard reflection, and can be measured with relative precision.

It is concluded from Table 17 that the differences in the 131 spacings are significant. There is, therefore, a small field of arsenopyrite solid solution at 600° C, which is presumed, by analogy with the related structures of loellingite and marcasite, to be elongated along the 1:2 cation-to-anion line. The measurements are a qualitative indication that the field of solid solution is very small. There is a large difference between the spacings shown and the 1.6307 Å value for Freiberg arsenopyrite whose composition lies on the arsenic-deficient side of ideal FeAsS.

Variation of Arsenopyrite Composition as a Function of Temperature

At each temperature of investigation, arsenopyrites were synthesized in two assemblages to show the maximum compositional variation. These data are given in Table 18. Runs attempted at lower temperatures were unsuccessful due to extremely slow reaction rates.

These data are presented diagrammatically in Figure 14. This is a projection of the pertinent ternary phase relations onto a 1 : 2 cation-to-anion section, with temperature and arsenopyrite 131 spacing as the axes. Although the quantitative relationship has not been determined, the 131 spacing is believed to be a sensitive measure of arsenopyrite composition. Therefore, each point shown in Figure 14 is precisely located relative to each of the other points, but its composition cannot be given in terms of percent iron, arsenic, and sulfur. On any given isotherm the maximum variation in arsenopyrite composition appears to be small; however, throughout the range of

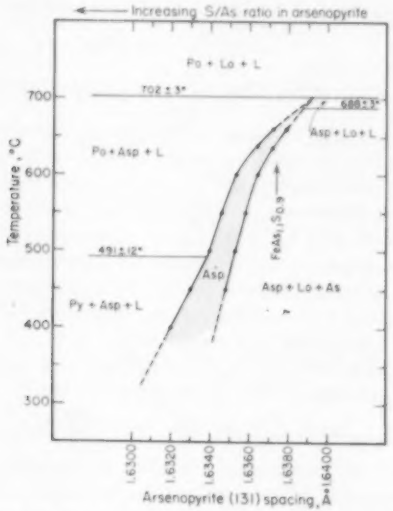

FIG. 14. Variation of the arsenopyrite composition as a function of temperature, indicated by measurements of the 131 spacing. The arsenopyrites were synthesized in silica tubes at "the vapor pressure of the system" from bulk compositions in the various univariant assemblages shown. It is estimated that arsenopyrite with the ideal composition (FeAsS) would have a 131 spacing in the 1.6335 to 1.6340 Å range.

temperatures investigated the total compositional variation is appreciable. The compositions richer in arsenic are stable only at the higher temperatures, those richer in sulfur only at the lower temperatures. To give an approximate quantitative comparison for the compositions involved in Figure 14, $FeAs_{1.1}S_{0.9}$ has a 131 value of 1.6372 Å while natural arsenopyrite with the approximate composition $FeAs_{0.95}S_{1.05}$ has the value 1.6307 Å.

A few preliminary runs indicate that confining pressure has a very marked effect on stabilizing the sulfur-rich arsenopyrite compositions. Arsenopyrites were synthesized in gold tubes at 2,070 bars confining pressure from bulk compositions in the arsenopyrite-pyrrhotite-liquid region. Those grown

at 600° and 500° C had 131 spacings of 1.6328 and 1.6315 Å, respectively. These values indicate arsenopyrite compositions relatively much richer in sulfur than the values at the corresponding temperatures in Figure 14, where the pressure was very low ("vapor pressure of the system"). Therefore, either lower temperature at fixed pressure, or higher confining pressures at a given temperature, favor the growth of arsenopyrites with sulfur-rich compositions. Both low temperature and high confining pressure in combination are required to produce the maximum sulfur substitution for arsenic in arsenopyrite.

In all these experiments on the composition of arsenopyrite, the arsenopyrite was always synthesized from starting materials such as Fe_2As or FeAs plus an As-S glass. Therefore, the arsenopyrite actually grew under the chemical and physical conditions of the run and had a composition peculiar to those conditions of formation. On the other hand, once arsenopyrite has grown with a given composition it can then be heated for long periods of time under any other physical and chemical conditions within the arsenopyrite stability range, and its composition will not readily equilibrate to the new conditions. As is shown in Table 19, after heating for nearly 1 year at 550° C the arsenopyrite composition has barely begun to equilibrate with the new assemblage. This may be taken as an indication that the free energy of formation, and hence the motive force for reaction, does not vary appreciably with changes in composition of arsenopyrite solid solutions.

ARSENOPYRITE CRYSTALLOGRAPHY

The indices given in the literature for arsenopyrite powder diffraction patterns were based on cells which were geometrically orthorhombic. These indices did not account for the additional reflections and peak splitting that appeared in the diffraction patterns made by the writer, especially for some natural materials. Freiberg arsenopyrite was selected for further study of the indexing. The following pseudo-monoclinic cell dimensions in Ångströms, were derived from the powder pattern using the least-squares technique: $a = 5.744 \pm 0.002$, $b = 5.675 \pm 0.001$, $c = 5.785 \pm 0.002$, and $\beta = 112° 10' \pm 3'$. Indexing (23) based on this cell accounted for all the observed reflections in the arsenopyrite powder diffraction pattern. Morimoto (63) showed that this material had triclinic symmetry ($C_1^1 - P1$); however, the α and γ angles were extremely close to 90°.

The arsenopyrites synthesized in the present study, with compositions near $FeAs_{1.1}S_{0.9}$, are more arsenic-rich than the Freiberg material (Table 19). Although the powder diffraction patterns of these materials are similar in the gross aspect, only the natural material shows splitting of some of the reflections. Indexing based on a pseudo-orthorhombic cell would probably account for all the reflections observed for synthetic arsenopyrite; nevertheless, the pseudo-monoclinic indexing was retained for clarity and ease of comparison. The cell values for synthetic arsenopyrite, unrefined by the least-squares method, are: $a = c = 5.79_6 \pm 0.01$ Å, $b = 5.72_0 \pm 0.01$ Å, and $\beta = 113° 21' \pm 10'$.

EXPERIMENTS ON NATURAL ARSENOPYRITE

A successful method of synthesizing pure arsenopyrite was described. It was employed only at temperatures of 600° C and higher in order to obtain complete reaction in a matter of a few weeks. Since the arsenopyrite stability field is limited and does not extend to FeAsS composition at these temperatures, the only arsenopyrites that one can synthesize, to give a product free from other phases for subsequent use in other experiments, have compositions in a narrow range around $FeAs_{1.1}S_{0.9}$. It was desirable to check some reactions using arsenopyrite with a more sulfur-rich composition. Such compositions are common in natural arsenopyrites, and the Freiberg material was found, after examination and analysis, to be suitable.

Chemical Analysis of a Natural Arsenopyrite

Chemical analysis was necessary in order to determine, first, the arsenopyrite composition, and second, the total composition to be used in the experiments. In order that the analysis would be a reliable measure of the arsenopyrite composition, considerable care was taken in selection of the sample to insure its freedom from extraneous phases.

In addition to arsenopyrite, the original Freiberg specimen contained some quartz, chalcopyrite, and galena. The specimen was very coarsely crushed and hand picked. The galena was coarse grained and presented no separation problem. The chalcopyrite occurred in fine veinlets. Only arsenopyrite fragments apparently free from impurities were chosen. When six of these 0.5 to 2.0 mm fragments were mounted and polished, examination showed that two contained veinlets of chalcopyrite with galena. The total chalcopyrite was estimated to be less than 0.1 percent and the galena much less. After 90 seconds of etching in saturated $FeCl_3$ solution no loellingite was detected. The arsenopyrite fragments in the sample were each recrushed into several parts. Any grains that contained chalcopyrite detectable with a 30× binocular microscope were discarded. Approximately 2 g of the selected arsenopyrite was sent to the analysts.

The sample was chemically analyzed for Fe, As, S, Co, Ni, Bi, and Cu by Drs. H. B. Wiik and Paavo Väänänen, Helsinki, Finland. Insoluble SiO_2 was also reported. The results are shown in Table 20.

The high purity of the material made it suitable for use in the experimental studies. The 0.15 percent copper is attributed to chalcopyrite that escaped detection due to inclusion within the arsenopyrite although some copper may have been in solid solution. The effect of this copper on the experimental results was assumed to be negligible.

This natural arsenopyrite, with the composition $FeAs_{0.97}S_{1.06}$, is sulfur rich [43] relative to the theoretical formula FeAsS. By comparison, the syn-

[43] The analyzed values shown in Table 19 contain errors that cannot be evaluated. However, if one assumes errors of 0.1, or even 0.2, percent in the arsenic and sulfur analyses, these are small compared with apparently real differences of 1.68 and 1.20 percent between the analyzed values for Freiberg arsenopyrite and the theoretical values for FeAsS.

TABLE 19

Data Showing the Ability of Arsenopyrite, Once Synthesized, to Maintain its Composition out of Equilibrium with a New Environment

Starting materials	T, °C	Time, days	Phases present	d131 Å
$FeAs_2$ + $As_{.77}S_{.23}$	635	42	Asp + Lo + As + V	1.6372 ± 0.0002
FeS_2 + Asp from above run	550	304	Asp + Po + L + V	1.6367 ± 0.0003
Fe_2As + $As_{.50}S_{.50}$	550	84	Asp + Po + L + V	1.6346 ± 0.0002

TABLE 20

Analysis* of Natural Arsenopyrite from Freiberg, Germany
(Values in Weight Percent)

	Reported values	Copper subtracted as chalcopyrite and remainder recalculated to 100 percent	Ideal FeAsS
Fe	34.34	34.41	34.30
Cu	0.00		
Ti	0.00		
As	44.33	44.58	46.01
Sb	0.00		
S	20.89	21.01	19.69
Ni	0.15		
SiO_2	none detected		
Total	99.71†	100.00	100.00
Relative atomic ratio		1 : 0.966 : 1.063	
Relative cation-to-anion ratio		1 : 2.029	

*Chemical analysis performed by H. H. Hilk and P. Hänchen.

Semiquantitative spectrographic analysis showed the total of all other impurities to be about 0.1 percent.

TABLE 21

Data Establishing the Invariant Temperature of Natural Arsenopyrite

In each run an $As_{.71}S_{.29}$ glass was combined with natural arsenopyrite to yield a bulk composition lying in the Asp + Po + L + V region.

T, °C	Time, days	Phases present
696.2	3	Asp + Po + L + V
700.5	4	Asp + Po + L + V
703.5	3	Po + Lo + Asp* + L + V
705.0	4	Po + Lo + L + V

*Very minor amount resulting from lack of equilibrium due to temperature fluctuations in 1° range or insufficient time to equilibrate.

TABLE 22

Data Showing the Reluctance of Diverse Arsenopyrite Compositions to Approach an Equilibrium Value under Identical Conditions

Starting materials	T, °C	Time, days	Phases present	d131 Å
$FeAs_{1.1}S_{0.9}$ + $As_{.71}S_{.29}$	690	83	Asp + Po + L + V	1.6358 ± 0.0002
Natural arsenopyrite ($FeAs_{0.995}S_{1.005}$) + $As_{.71}S_{.29}$	690	83	Asp + Po + L + V	1.6324 ± 0.0003
Natural arsenopyrite before heating				1.6304 ± 0.0002
Synthetic arsenopyrite before heating				1.6355 ± 0.0002

thetic arsenopyrite grown at 660° C, previously shown in Table 16, has the composition $FeAs_{1.10}S_{0.90}$ and is arsenic rich relative to FeAsS.

Differential Thermal Analysis of Arsenopyrite

To investigate the possibility that a reversible, nonquenchable phase transition, such as disordering at elevated temperatures, in either natural or synthetic arsenopyrite might underly the observed differences in the X-ray powder patterns, both materials were subjected to differential thermal analysis. The natural and synthetic arsenopyrites were studied through the temperature ranges 30° to 616° C and 30° to 626° C, respectively. In neither case was there any indication of a thermal effect in the d.t.a. record. This is taken as reasonably strong evidence that transformations do not occur in arsenopyrite in these temperature ranges. It is concluded that the observed differences of X-ray powder diffraction patterns between natural and synthetic arsenopyrites is a function of compositional difference and not a high-low crystallographic transition.

Determination of Invariant Temperature Using Natural Arsenopyrite

When the temperature of the arsenopyrite invariant point was determined, synthetic, arsenic-rich arsenopyrite was employed. Theoretically, as the arsenopyrite invariant point is approached along any of the univariant curves, the arsenopyrite compositions shift toward a common value at the invariant point. However, evidence was presented which showed that the composition of an arsenopyrite would not shift in response to a change in environment within a reasonable length of time. Therefore, the arsenopyrite invariant temperature determination was repeated using the sulfur-rich Freiberg arsenopyrite to see if a different temperature value would be obtained. However, no difference was observed. As is shown in Table 21, the invariant temperature is 703° ± 3° C. This agrees with the value of 702° ± 3° C found with synthetic arsenopyrite (Table 9). The compositional differences between the synthetic and the natural arsenopyrites, as indicated by the peculiarities of their individual X-ray patterns, remained unchanged up to the breakdown temperature.

Other Experiments on the Stability of Particular Arsenopyrite Compositions

Natural and synthetic arsenopyrites were combined with As-S glasses, in separate runs, to give bulk compositions on the arsenopyrite-pyrrhotite-liquid-vapor univariant curve. Hence, if both runs were heated at any given temperature the arsenopyrite in each run should, theoretically, shift to a common equilibrium value for that temperature and assemblage. This test was conducted at a temperature as close to the melting point as was practical, in order to aid the diffusion process as much as possible. Even after heating for 83 days under these conditions, the two arsenopyrite compositions, as indicated by their 131 spacings shown in Table 22, have barely begun to

approach a common value. In a polished section of a portion of the latter charge, some of the fragments appeared to have retained their original angular shape, and under cross-polarized light a fringe of fine grains was observed around a large grain which was otherwise a single crystal. The fringe was interpreted as being recrystallized equilibrium arsenopyrite. The layer was too thin to separate and X-ray independently.

In another attempt to change the properties of natural arsenopyrite some of the Freiberg material was heated 2 days at 750° C in a sealed silica tube. The arsenopyrite melted to loellingite, pyrrhotite, liquid, and vapor. The run was further heated 21 days at 680° C to grow arsenopyrite from the breakdown products. While not at equilibrium, 60 to 70 percent arsenopyrite had crystallized from the breakdown products. It gave an X-ray powder diffraction pattern indistinguishable from synthetic arsenopyrite, and the 131 spacing was 1.6370 ± 0.0002 Å. This is essentially the same as the value of 1.6373 ± 0.0002 Å for synthetic arsenopyrite grown at 660° C.

GEOLOGICAL IMPLICATIONS AND APPLICABILITY OF THE EXPERIMENTAL DATA TO THE STUDY OF ORES

In both natural and artificial systems the coexisting phases are determined only by (1) the temperature, (2) the pressures, and (3) the relative atomic proportions. The range of reaction temperatures extends to lower values in nature than can generally be investigated successfully in the laboratory. Nevertheless, the laboratory data can, in some instances, be extrapolated to lower temperatures using P-T projections. The pressure term involves consideration of both the partial pressures and the total confining pressure. Compositionally the synthetic system is simple relative to the environments of ore deposition. Until many related synthetic systems are investigated, there are certain simplifying assumptions and limitations required in the application of the experimental data from the Fe-As-S system to ore studies.

Many components, in addition to those present in this system, occur in the environment of ore deposition. However, their presence will not affect the phase relations concerned unless they enter into the composition of one or more of the condensed phases. On the other hand, where water, for example, is soluble in a melt, its presence will lower the melting temperature of that phase.

Published chemical analyses, and Fleischer's (29) minor element compilation, give some indication of the principal elements that are soluble in arsenopyrite. (In some instances this also applies to loellingite, pyrite, and pyrrhotite.) Cobalt is the most common and its substitution for iron may form a complete solid solution series from arsenopyrite to glaucodot [(Co,Fe)AsS]; however, more than 70 percent of the reported analyses contain less than 0.5 percent cobalt. Other elements, if present, are generally in concentrations of only a few hundredths of 1 percent, and the following are approximate maximum values for their concentration in arsenopyrite; bismuth 1.0 percent, nickel 0.3, manganese 0.3, antimony 0.2, and selenium 0.07.

Solubility of copper is possible, but the data are inconclusive since chalcopyrite is often present in the analyzed materials. The effect on the phase relations of these trace elements should be investigated. However, the findings of workers in other systems (53, 1) generally support the present assumption that less than 1 percent of a foreign element in solid solution in one of the minerals of the Fe-As-S system will have an effect on the phase relations which is within the limits of error claimed for the pure system.

The experimental data have some interesting applications. (a) Phase equilibrium [44] is suggested in a natural mineral assemblage that contains the same phases as a synthetic equilibrium assemblage. (b) The stability limits determined for some of the assemblages can give a measure of the physical conditions that prevailed during deposition. (c) The limits established for arsenic and sulfur substitution in arsenopyrite and for sulfur substitution in loellingite may be used to make estimates of formation temperatures.

A few specific examples may help to clarify the application of the data. (1) Whenever arsenopyrite occurs it is known that the temperature of formation was below 702° ± 3° C. This value is subject to a small positive correction with increased confining pressure as long as the sum of the partial pressures (or activities) of arsenic and sulfur equals the total pressure. In nature, other volatiles such as water also contribute to the total pressure. Therefore, if another volatile component is soluble in the breakdown liquid, the temperature limit of arsenopyrite existence for a given total pressure is presumably lower than the upper stability curve. And, within fairly broad limits, 702° C can be considered as the maximum temperature of formation for naturally occurring arsenopyrite.

(2) If native arsenic coexists with arsenopyrite the deposition temperature was below 688° ± 3° C. The effect of confining pressure will be similar to that just discussed.

(3) If pyrite coexists with arsenopyrite in the presence of vapor, at least one member of the mineral pair was deposited below 491° ± 12° C. On the other hand, at a confining pressure of 1,035 bars, pyrite and arsenopyrite can coexist at temperatures up to 509° ± 10° C, provided that at 509° C the combined partial pressures of sulfur and arsenic equal the confining pressure. It is unlikely that sulfur and arsenic partial pressures or activities are anywhere near that great in the natural environment of ore deposition. It should also be noted that the slope of the upper stability curve for this assemblage is only about 1.8° C/100 bars. For these reasons, the maximum temperature of pyrite-arsenopyrite coexistence in nature must be within the limit of error of the invariant temperature, 491° ± 12° C. Regardless of the fact that pyrite is stable up to 743° C and arsenopyrite up to 702° C, the two minerals are not stable as a pair above approximately 491° C. The same values apply whether or not pyrrhotite coexists with the pyrite and arsenopyrite.

[44] Where there is nonequilibrium between two or more ore minerals the evidence such as reaction rims or compositional zoning is usually more easily found than is evidence of equilibrium when it occurs. Nevertheless, phase equilibrium is usually claimed when the minerals are in physical contact with no separating reaction rims.

A few exploratory experiments were conducted to test the reaction Py + Asp → Po + L in the presence of water at a total confining pressure of 2,070 bars. The temperature at which the reaction would proceed was not measurably affected (537° C, Table 13) by the presence of the water. This is interpreted as an indication of very low mutual solubilities between water and the Fe-As-S phases under these physical conditions. It is not known whether other volatiles such as CO_2 would have any appreciable lowering effect on the pyrite-arsenopyrite stability. The reverse reaction Po + L → Py + Asp was not investigated in the presence of water.

Natural Assemblages of Fe-As-S Minerals

To make some first-hand observations on the relations of natural arsenopyrite with iron-sulfur and/or iron-arsenic minerals, polished surfaces were prepared on ore specimens from various parts of the world. The specimens commonly contained ore minerals unrelated to the Fe-As-S system, which were identified in many cases but were not studied in detail.

A suite of nine specimens from the Giant Yellowknife Mine, North West Territories, was obtained from Dr. L. C. Coleman, Ohio State University, Columbus. Coleman (24) studied the mineralogy of this ore and made sphalerite temperature estimates through application of the FeS-ZnS solvus curve of Kullerud (53). The temperatures in seven specimens ranged from 375° to 555° C with the three highest values being 485°, 510°, and 555° C. Coleman did not indicate whether or not pyrrhotite was present with the sphalerite in the above specimens. If pyrrhotite was not present the above temperatures would only represent minimum values. The writer observed no pyrrhotite in the nine specimens examined; however, only two of these were among the seven specimens on which Coleman made temperature determinations.

All the specimens examined by the writer contained pyrite. Arsenopyrite was observed in seven of the nine specimens, always in intimate contact with the pyrite, and in several instances arsenopyrite inclusions up to 10 microns across were observed in the pyrite. No pyrite inclusions were observed in the arsenopyrite. On this basis one might tentatively assume that the arsenopyrite was older than the pyrite. This was also Coleman's conclusion although he stated that the evidence was indefinite. In any case, the temperature was below 491° ± 12° C [45] before the minerals formed together. Only two of Coleman's sphalerite temperatures are much above 491° C. The specimen which gave a sphalerite temperature of 555° C was not available to determine whether or not pyrite and arsenopyrite coexisted. In the 510° C specimen pyrite and arsenopyrite were in intimate contact. Here the temperature discrepancy is small enough to be covered by possible errors in the methods [46] or a difference in the effect of confining pressure.

[45] A pressure effect need not be included (see discussion on preceding pages). Also Coleman's sphalerite temperatures are not corrected for pressure.

[46] Particularly since Coleman (24) had to use the cell sizes to determine the FeS contents in the sphalerites, and had to make cadmium and manganese corrections for these values.

A second suite of ten specimens was provided by Drs. F. Leutwein and O. Oelsner of the Mineralogisches Institut, Freiberg, from the Freiberg area and the surrounding arsenic metallogenic province. All of the nine polished surfaces examined contained arsenopyrite. Pyrite, which occurred in six of these specimens, was in contact with the arsenopyrite. In one instance pyrite veins cut the arsenopyrite, and generally the pyrite conformed to the euhedral outlines of the arsenopyrite wedges. This evidence may be taken to indicate that pyrite is the younger of the two. The formation temperature for these minerals, at least for pyrite, was below 491° C. The other ore minerals observed, which apparently formed later, were chalcopyrite, sphalerite, galena, and traces of marcasite and pyrrhotite.

Three specimens from the Parrex prospect, Hanson Lake, Saskatchewan, were furnished by Dr. A. R. Byers of the University of Saskatchewan, Saskatoon. The specimens all contained arsenopyrite, and two also contained pyrite. In both of these cases inclusions of arsenopyrite were observed within pyrite grains and showed no reaction rims. Therefore, either the younger of the two minerals, or both minerals, formed below 491° C. Other minerals contained in the specimens were: sphalerite, galena, chalcopyrite, and lesser amounts of pyrrhotite, bournonite, and very minor tetrahedrite (not positively identified). In the specimen without pyrite, marcasite was observed in irregular veins and patches that cut all the other sulfide minerals. Aside from the very late marcasite, the other sulfide minerals showed few criteria for relative ages. This led the writer to believe that all these minerals may have been of very similar age. Byers (18) studied specimens from the same prospect and gave the following relative ages: arsenopyrite and pyrite, followed successively by pyrrhotite, sphalerite, galena, and chalcopyrite. The cell constant for the sphalerite in one specimen was determined as $a = 5.415_8$ Å. This cell size gave an FeS content of approximately 13.7 mole percent when plotted on the determinative curve of Skinner, Barton, and Kullerud (83). This FeS content, when plotted on Kullerud's (53) ZnS-FeS solvus curve, gave the apparent sphalerite formation temperature as 440° C. The contents of CdS and MnS in solid solution in the sphalerite are unknown. Since Cd and Mn expand the ZnS cell, if these elements are present, the true formation temperature will be lower than the measured apparent temperature. Solid solution of CuS in an iron-bearing sphalerite causes a reduction in the cell size (Dr. P. Toulmin, U. S. Geological Survey, personal communication, 1959). Lack of equilibrium with pyrrhotite has the same effect, and hence both factors will tend to make the true temperature greater than the above apparent temperature value. In any case, it would seem that the sphalerite formed well below 491° C as did one, or both, minerals of the pyrite-arsenopyrite pair.

One specimen was examined from the Morro Velho Mine, Brazil. It was obtained from Dr. J. E. Gair of the U. S. Geological Survey, Denver, Colorado. It contained abundant arsenopyrite and pyrrhotite, with a small amount of later pyrite. The pyrrhotite was intermediate in relative age, and it occurred as irregular, intergranular masses between the grains of arsenopyrite and gangue minerals. The ratio of the sulfur-to-arsenic partial

pressures apparently increased during deposition of the pyrrhotite plus arsenopyrite, which culminated in deposition of the additional phase pyrite.

A specimen from the New Consols Mine, Cornwall, described by Embrey (27) was obtained from the British Museum, London (BM1958, 403). The specimen contained both arsenopyrite and loellingite in the proportion of about 2 or 3 to 1 as indicated by the relative intensities in the X-ray powder diffraction patterns. The minerals could not be clearly distinguished in polished section. The specimen contained accessory cassiterite. The arsenopyrite had a 131 spacing of 1.6347 Å. When this value is plotted on the arsenic-rich solvus curve for arsenopyrite (Fig. 14), a formation temperature between 400° and 500° C is indicated.[47] X-ray measurements on the coexisting loellingite indicated a sulfur content of about 1.4 weight percent. While the solvus curve has not been determined, this is much less sulfur than the maximum of 3.4 percent soluble in loellingite at 702° C. Thus, the formation temperature for this natural loellingite was well below 702° C.

Possible Arsenopyrite-Gold Correlation in Ore Deposition

Due to the effects of gold on the stability of arsenopyrite an attempt to determine the upper stability curve for arsenopyrite using gold sample containers was unsuccessful; however, unexpected data were provided which bear on the gold-arsenopyrite relations in nature.

Gold can diffuse rather readily through arsenopyrite at temperatures of 660° C and higher. In 4-hour runs, gold from the tube walls diffused through and saturated the arsenopyrite charges which were approximately 1 mm thick. Polished sections of these charges showed 5 areal percent, or more, of gold deposited as irregular grains throughout the charge (Fig. 11). Since, under those conditions, solid arsenopyrite and gold were the only phases present, solid state diffusion was involved. This diffusion would probably be mostly of the grain boundary type. It also seems possible that there was some diffusion through or into the crystals. As shown earlier in Table 16, the solid solubility of gold in arsenopyrite, synthesized in silica tubes at 600° C, is insufficient to measurably affect the 131 spacing in the quenched product. However, this may not exclude the possibility of a small gold solubility in arsenopyrite, for example 0.1 percent (approximately 30 oz/ton of arsenopyrite) or less. This amount would, nevertheless, be of great interest in economic geology. Also dissolved gold might exsolve into submicroscopic inclusions during quenching and would not affect the 131 spacing.

Of necessity this discussion is speculative, because the precise determination of the solubility of gold in arsenopyrite as a function of temperature, along with the attendant experimental problems, would itself be a major study. The literature on gold ores contains mutually supporting evidence. Arsenopyrite occurs abundantly in a great many gold deposits, but the direct

[47] This crude estimate of formation temperature does not include corrections for confining pressure, which would be positive, or corrections for elements other than Fe, As, and S, if present.

relation between gold and arsenopyrite is not always obvious. Interpretation of these ores would be aided by a clear demonstration that gold is soluble in arsenopyrite at elevated temperatures, and as the ore cools the limit of gold solubility in arsenopyrite decreases. Since diffusion rates are relatively high, the gold that comes out of solid solution is able to diffuse to the edges of the arsenopyrite grains, thus they show no typical exsolution textures.

Concerning the gold relations at the Giant Yellowknife Mine, Coleman (24, p. 413–414) stated: "The most common association of gold in the Giant ores is with arsenopyrite. The gold generally either fills fractures in, or forms thin coatings on, arsenopyrite crystals." Coleman also believed that the coarse gold observed represented original fine gold that had been reworked by later mineralizing fluids. In studying the size distribution of the gold particles, he found a substantial proportion that approached the submicroscopic and colloidal ranges. Coleman (24, p. 419) tentatively concluded that much of the fine-grained gold had been in solid solution in the sulfides at one time and was aggregated by an "auto-annealing" process. The same idea was expressed in a 1946 report by the Staff of the Lake Shore Mine (84), Ontario, in connection with their ore. The possibility of minor amounts of gold solid solution in pyrite has been proposed by several investigators, Burg (17), Kuranti (56), Maslenitsky (58), and Stillwell and Edwards (86). The possibility of gold solid solution in arsenopyrite has received less attention. Stillwell and Edwards (86), who studied "invisible gold" in pyrite at the Dolphin East lode, Tavua, Fiji, reported that there was more invisible gold in the arsenopyrite than in the pyrite (i.e. over 30 oz of gold per ton of arsenopyrite). Edwards (25, p. 169) discussed a polished section of arsenopyrite (25, Fig. 156) from the Bon Accord Mine, Yackandandah, Victoria, which showed numerous tiny gold inclusions, often only 10 microns across and smaller. This might be taken as an example of exsolved gold. In 1958 Edwards (26) studied the Maude and Yellow Girl gold ore from Glen Wills, Victoria, and stated that 10 percent of the gold present was in solid solution in the arsenopyrite. He did very fine grinding and still got some "invisible" gold which was unrecoverable by cyanidation and which concentrated with the sulfides. From "practically pure" fractions of arsenopyrite and pyrite he obtained assays of 6 and 2 oz of gold per ton (approximately 0.02 and 0.007 percent), respectively. Since this gold could not be seen with the aid of a reflecting microscope, Edwards assumed it was in solid solution in the arsenopyrite. This assumption is not justified, but his results are very interesting.

In 1944 Schwartz (81) considered in some detail the nature of the relations between gold and its associated minerals. Of the 115 districts for which Schwartz reviewed the literature, 45 had native gold described as directly related to arsenopyrite. He added that in several other districts arsenopyrite was present in the ore but no direct relationship was described. The essence of Schwartz's summation was (p. 404):

"As a result of a comprehensive review of the literature as well as personal studies, the writer is impressed with the small amount of replacement

of the minerals with which gold is associated. Gold does occasionally replace the host minerals but certainly this is the exception rather than the rule. . . . It is difficult to see how a mineral could act as an effective precipitant unless it entered into the reaction. If it did react then the minerals being precipitated including gold, should replace the host minerals, unless the precipitation is indirect."

In the light of the present hypothesis, one can avoid the necessity of gold replacing the host mineral, arsenopyrite, in each of the following instances: (1) the gold came in at the same time as the arsenopyrite and was deposited in solid solution in the arsenopyrite, or (2) the gold came in later than the arsenopyrite, and those arsenopyrite grains that were not shielded from the gold-bearing solutions "soaked" up the gold in solid solution. In either case, as the ore mass later cooled, the gold exsolved and migrated to the edges of the arsenopyrite grains, and possibly was locally reworked by later mineralizing fluids. There need be no apparent replacement of the arsenopyrite. If, due to external forces, the arsenopyrite was fractured during cooling, such a fracture could localize the diffusion of gold out of solid solution. This would currently be interpreted as a later veinlet of gold cutting the arsenopyrite.

In summation this hypothesis depends only upon the observation that at high temperature gold can, in the solid state, diffuse rapidly through arsenopyrite. From this it is inferred that sufficient gold may be soluble in arsenopyrite, at elevated temperatures, to satisfy the needs of many gold ore deposits.

FEATURES IN THE Fe-AS-S SYSTEM THAT MERIT FURTHER INVESTIGATION

The solvus curve that defines the limit of sulfur solubility in loellingite while in coexistence with arsenopyrite was not determined; however, the trend at high temperature was outlined. It is probable that this solvus curve, if accurately located, could be used in geothermometry to estimate the formation temperature of loellingite where this mineral coexists with arsenopyrite. In those instances where arsenopyrite was not present the sulfur content of the loellingite would give a minimum value of formation temperature.

Confining pressure appears to have a marked effect on the compositions of synthetic arsenopyrites. A detailed study of this phenomenon, though involving some technical difficulties, might be very fruitful. It is also possible that the composition of natural arsenopyrite in arsenopyrite-pyrite or arsenopyrite-loellingite mineral pairs can give some measure of the deposition temperature or deposition pressure if the temperature is known independently.

Numerous X-ray measurements have shown that the positions of some reflections from arsenopyrite vary considerably as a function of composition. It would be possible, using 10 or 20 chemically analyzed, natural specimens, which contain only Fe, As, and S, to establish determinative curves of composition versus X-ray spacings, or cell constants.

Cobalt, and to a lesser extent some other elements, can substitute in some of the minerals of the Fe-As-S system. These should be investigated as to the amount of possible substitution, the effect of such substitutions on the

reaction temperatures governing the assemblages, and the shapes of the solvus surfaces produced.

CONCLUSIONS

Since economic geologists are among the principal beneficiaries of a study such as this, the following is a brief resumé of those findings of most interest in ore petrology.

The composition of arsenopyrite varies with temperature, and the precise limits are unknown. However, at any given fixed temperature and pressure, the total compositional variation is very small. Arsenopyrites synthesized in silica tubes in the 630° to 650° C range have the composition $FeAs_{1.1}S_{0.9}$. More sulfur-rich arsenopyrites become stable as lower temperatures are employed, at least down to 400° C. Synthesis under confining pressure further shifts the stability field in the sulfur-rich direction. The sulfur-rich limit of the arsenopyrite field of solid solution must lie beyond $FeAs_{0.97}S_{1.06}$, which is the composition of a sulfur-rich natural arsenopyrite that was chemically analyzed. Most natural arsenopyrites tend to be sulfur rich as indicated by published analyses. There may be variations of smaller magnitude in the cation-to-anion ratios, but these are more difficult to demonstrate.

Aside from the ZnS-FeS (53) and $Fe_{1-x}S$-FeS_2 (2) solvus curves, which are of fairly wide application, the ore petrologist has few reliable indicators of formation temperatures for sulfide minerals or mineral assemblages. A variety of additional methods are given in a review by Ingerson (45). In the present study it has been shown that pyrite and arsenopyrite cannot coexist above 491° ± 12° C; hence, their occurrence together in a deposit indicates that one or both of these minerals formed below that temperature. Similarly, the incongruent melting temperature of arsenopyrite at 702° ± 3° C fixes the upper limit of its formation in a deposit. A considerable solid solubility of sulfur in loellingite has been demonstrated. The loellingite solvus with arsenopyrite and the arsenopyrite solvus curves with loellingite or pyrite are possible geothermometers.

Pressure runs with arsenopyrite in gold tubes show that gold diffuses readily through arsenopyrite at temperatures of 600° to 700° C, which suggests a small amount of solid solubility at elevated temperatures. This bears on the frequent association of gold and arsenopyrite in ores. I believe that in many such deposits much of the gold was originally emplaced as a solid solution in the arsenopyrite and subsequently diffused out of (exsolved from) the arsenopyrite as the ore mass cooled.

ACKNOWLEDGMENTS

The entire study was done at the Geophysical Laboratory, Carnegie Institution of Washington, using the laboratory facilities of Dr. Gunar Kullerud, to whom I am also indebted for generous guidance given in all phases of the experimental study and manuscript preparation. I am grateful to Dr. N. Morimoto for X-ray single-crystal data on arsenopyrite, to Drs. H. S. Yoder and E. H. Roseboom for constructive discussions during the study and

critical reading of the manuscript, and to Dr. R. A. Yund for comments on the manuscript. My gratitude is expressed to Dr. J. S. Stevenson, McGill University, Montreal, for advisory assistance, and to Drs. H. B. Wiik and P. Väänänen, Helsinki, for chemical analyses of two arsenopyrites.

The ore and mineral specimens used in this study were obtained from: The Smithsonian Institution, Washington, through the cooperation of Mr. P. E. Desautels; the British Museum (Natural History), London, through the kindness of Dr. P. G. Embrey; Dr. A. R. Byers, University of Saskatchewan, Saskatoon; Dr. L. C. Coleman, Ohio State University, Columbus; Dr. J. E. Gair, U. S. Geological Survey, Denver; and Drs. F. Leutwein and O. Oelsner, Mineralogisches Institut, Freiberg.

I am especially grateful to the National Research Council of Canada whose financial support for two years made the study possible.

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March 14, 1960

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Economic Geology
Vol. 55, 1960, pp. 1653–1675

THORIUM, URANIUM AND ZIRCONIUM CONCENTRATIONS IN BAUXITE[1]

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ABSTRACT

Twenty-nine samples of bauxites from different locations were analyzed for thorium and uranium by gamma-ray spectrometric, alpha counting, and wet chemical methods. The thorium concentrations range from 5.0 to 131 ppm and average 48.9 ppm. The uranium concentrations range from 2.7 to 26.7 ppm and average 11.4 ppm. The thorium-to-uranium ratios range from 1.5 to 20.9, with an average value of 5.1. Zirconium determinations on some of the bauxites gave values ranging from 0.02 to 0.65 percent Zr, and averaging 0.09 percent Zr.

The thorium, uranium and zirconium contents of the bauxites are related to the type of source rock. Bauxites derived from nepheline syenites contain more thorium and uranium than bauxites derived from other rock types; bauxites derived from basic igneous rocks have the lowest thorium and uranium concentrations, and bauxites derived from carbonate rocks have the lowest thorium-to-uranium ratios. The greatest concentrations of Zr were found in bauxites derived from nepheline syenites, and bauxites derived from carbonates contained the lowest concentrations of Zr.

A study of samples from alumina plants treating Surinam and Arkansas bauxites shows that during the process, over 70 percent of the thorium and uranium in these two bauxites is concentrated into the red mud, and the alumina contains very small amounts of these elements.

[1] Based in part on a study conducted by K. A. Richardson as part of the requirements for the degree of Master of Arts at Rice Institute.

This study also indicated that much of the thorium and uranium in bauxites occurs in either primary or secondary resistate minerals.

INTRODUCTION

For some time it has been known that certain bauxites contain greater amounts of thorium and uranium than the average crustal rocks. The primary purpose of this study was to make a general survey of bauxites to investigate the distribution of radioactive elements, and determine the significance of this distribution.

In addition to contributing to the geochemical knowledge of thorium and uranium, the results of this study may have some economic value. The possibility of by-product recovery of thorium is suggested, also the possible use of radiometry in prospecting for aluminum ore.

PREVIOUS WORK

Although no data regarding the absolute thorium and uranium contents of bauxites have been found in the literature, with the exception of recently published papers by Adams and others, there are a number of papers that give theoretical reasons to expect relatively high concentrations of these elements in bauxites, and a number of qualitative reports that support the theory.

The application of the concept of ionic potential to the behavior of elements during weathering has been discussed by Goldschmidt and, with particular reference to Arkansas bauxite, by Gordon and Murata. The latter paper verifies Goldschmidt's statement regarding the effect of bauxite formation on certain elements, showing beryllium, chromium, copper, gallium, lead, manganese, molybdenum, niobium, scandium, titanium, vanadium, yttrium and zirconium to be concentrated, and barium, calcium, lanthanum, magnesium and strontium to be depleted during the alteration of nepheline syenite to bauxite.

Figure 1 is a plot of the ionic radius against the ionic charge for a number of elements. Values for the ionic radii are taken from Ahrens. The diagonal lines on the figure are the lines of equal ionic potential used by Goldschmidt, and Gordon and Murata as the boundaries for the group of elements with intermediate ionic potential values that are precipitated in nature as hydrolyzates. Tetravalent thorium and uranium lie well within these boundaries; hexavalent uranium is near the field of elements which form soluble complex anions.

From consideration of the ionic potential alone, thorium should be concentrated in bauxites, whereas uranium might be oxidized and removed as the soluble uranyl ion, UO_2^{++}. Measuring the radioactivity of Arkansas bauxite by beta counting, Frederickson found an equivalent radium content of 13.1×10^{-12} grams/gram of bauxite. This is larger by approximately one order of magnitude than the average value for acid igneous rocks. Frederickson believed that uranium was introduced into the deposit as uranyl ions and concentrated by adsorption on the aluminum minerals.

Similarly, Lovering concludes from investigations of radioactive iron oxides that "colloidal ferric oxide hydrate" adsorbs uranyl ion, and thus removes uranium from solution. Most of the thorium minerals resist weathering and remain in their original form, but tetravalent thorium would also be removed from solution by ferric hydroxide. During crystallization of the ferric colloid adsorbed uranium is expelled and forms separate minerals. Heinrich discusses radioactive gossans and laterites briefly, agreeing with Lovering's conclusions.

Davidson states that some terra rossa deposits in Central Africa are significantly radioactive. The radioactive elements are again reportedly adsorbed on the iron hydroxides, but in contrast to the above authors, David-

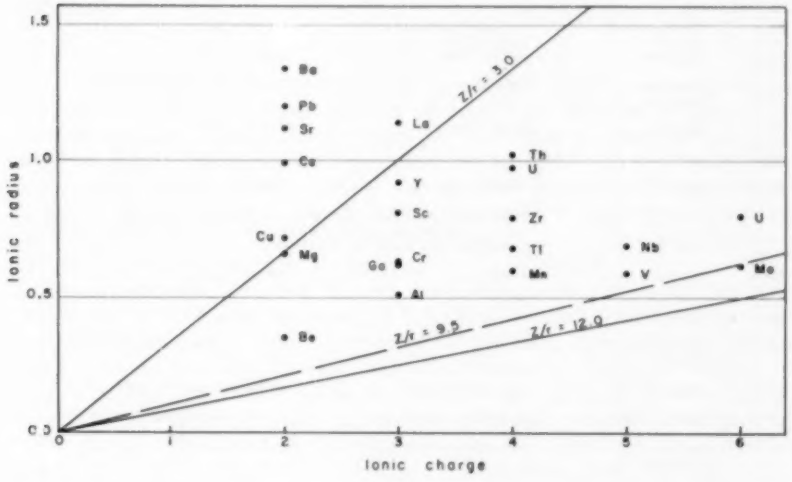

Figure 1. **Grouping of certain elements according to ionic potential.**

son believes that the parent uranium is largely leached and the radioactivity is due to thorium series and uranium series daughter elements.

Kiss and Mehes have studied Hungarian bauxites and reported their radioactivity. Using nuclear emulsions, Kiss detected a small amount of radioactivity in tabular inclusions within zircon crystals. Mehes, measuring radioactivity in the field, found a relationship between radioactivity and ore grade, with increased radioactivity also along lines of faulting and folding in the bauxite.

Occurrences of bauxites with uranium have been found in Yugoslavia, according to Ristic, which ". . . will apparently also become a source for the obtaining of uranium, because in the processing of aluminum, the uranium concentrates itself in the so-called red mud."

SAMPLES STUDIED

Samples of 29 bauxites (Table I) from different countries were analyzed for this study. It is thought that they constitute a fairly representative collection. Among the samples are bauxites derived from both acid and basic igneous rocks, metamorphic, clastic and carbonate sediments. Parent rocks of Irish and Jamaican bauxites were also analyzed. Table I lists the samples, giving their geographic location, known or inferred parent rock, and literature references.

Table I. List of Bauxite Samples

Sample	Location	Parent Rock	Reference
KR-1	French Guinea	nepheline syenite	Fermor (1915)
KR-2L	Gold Coast	volcanic ash	Cooper (1936)
KR-3 KR-3B	Dominican Republic	limestone	Goldich and Bergquist (1947)
KR-4 KR-4B KR-5L	Jamaica "	White limestone	Hartman (1955) Hill (1955)
KR-6L	Brazil	nepheline syenite	Teixeira (1942)
		Other parent rock types for Brazilian bauxites, reported in Fischer's (1955) bibliography, are: granite (Knecht), gneiss (Froes), schists (Goodchild) and phyllite (Guimaraes).	
KR-7L	British Guiana	diabase	Kersen (1955) Harrison (1910)
KR-8L	India	basalt	Fox (1923)
KR-9L	Bintan, East Indies	hornfels	Bemmelen (1941, 1949)
KR-10	Palau Islands	tertiary volcanics	Bridge and Goldich (1948)
KR-11L	Istria, Yugoslavia	mesozoic limestone	U.S. Bureau of Mines (1953)
KR-12L	Dalmatia, Yugoslavi	mesozoic limestone	Franotovic (1955)
KR-13L	Italy		Harder (1949)
KR-14L	France	mesozoic limestone	Lapparent (1949)
KR-15L	Greece	mesozoic limestone	Frantovic (1955)
KR-17L KR-18	Henry, Georgia Georgia	kaolinite	White and Benson (1952)
KR-20L	Oregon	miocene basalt	Allen (1948); Libbey, Lowry and Mason (1946)
KR-22	Mississippi	Porters Creek shale	Burchard (1924); Morse and Hand (1923)
KR-23L	Missouri	palaeozoic limestone	Keller (1944)
KR-26 KR-31	Surinam Surinam	igneous and metamorphic	Kersen (1955) Meulen (1949)
KR-27 KR-38	Arkansas Arkansas	nepheline syenite	Mead (1915)
KR-80 KR-83	Jamaica Jamaica	White limestone	(see KR-4, above)
KR-84	Antrim, Northern Ireland	basalt	Eyles (1952)

In addition to the individual bauxite samples, a suite collected on the Aluminum Company of America property at Bauxite, Arkansas, illustrates some of the types of bauxite deposits and stages in the development of bauxite from the nepheline syenite parent rock. A section of drill core from the same area, extending through the bauxite into the top of the syenite, was also studied.

To trace the radioactive elements through the processing of bauxite to alumina, material balance samples from two treatment plants were studied. These samples consisted of the feed bauxite, calcined alumina, red mud, and coarse sand, from plants operating on Surinam bauxite and on Arkansas bauxite.

The alpha activities of a number of aluminum metal samples were also measured.

ANALYTICAL METHODS

Thorium and uranium analyses were made for this study by gamma ray spectrometry, alpha counting, and wet chemical methods. All of the bauxite samples were analyzed by the gamma ray spectral method; some were checked by the alpha activity-fluorometric uranium method. All of the samples were alpha counted. One chemical thorium and a number of chemical zirconium determinations were made. Determinations of aluminum, iron, titanium, and silicon oxides presented in this paper are the routine analyses made by the Aluminum Company of America.

Approximately half of the gamma ray results were obtained at the Shell Development Company laboratory, Houston, Texas; other thorium and uranium spectrometer results presented in the paper were obtained at the Rice Institute. A full discussion of the spectrometry procedure is found in papers by Hurley; Adams, Richardson and Templeton and Whitfield, Rogers and Adams. Thorium was determined by measuring the 2.62 Mev gammas from thallium-208, uranium by measuring the 1.76 Mev gammas from bismuth-214, and thorium and uranium concentrations were both calculated from counts made on a channel centered at 0.61 Mev. Potassium was determined for some samples, using the 1.47 Mev gammas given off by potassium-40. Potassium content of bauxite is low, but the measurements were conveniently obtained, and are therefore included (Table IX).

Individual limits of error for the gamma ray spectral values are not given. The number of events recorded for each measurement was sufficient to give a statistical error of less than $\pm$ 5 percent. Additional sources of inaccuracy are the "physical errors" inherent in this method, and the possible inhomogeneity of the samples. A result of the very high thorium concentration in bauxites is the smaller error in thorium measurements. Ninety percent of the chemical thorium analyses made by Pliler agree to within 10 percent with the gamma ray measurements. However, the accuracy of the uranium measurement suffers from the increased thorium contribution to counts made at 1.76 Mev. Uranium measurements are judged accurate to well within $\pm$ 20 percent, the greatest inaccuracy being in samples with high thorium-

to-uranium (Th/U) ratios. Potassium measurements are considered to be accurate to within ± 5 percent of the amount present.

Calculation of thorium and uranium concentrations from thallium-208 and bismuth-214 gamma activity is based on the assumption that the thorium and uranium decay series are in secular radioactive equilibrium. Determinations of thorium and uranium by two independent methods showed samples of Arkansas and Surinam bauxites to be in equilibrium, but the fluorometric uranium procedure does not apply well to bauxites, due to (i) the difficulty in extracting all of the uranium from the sample, and (ii) interference of the high iron content of many bauxites with the fluorescence. However, a

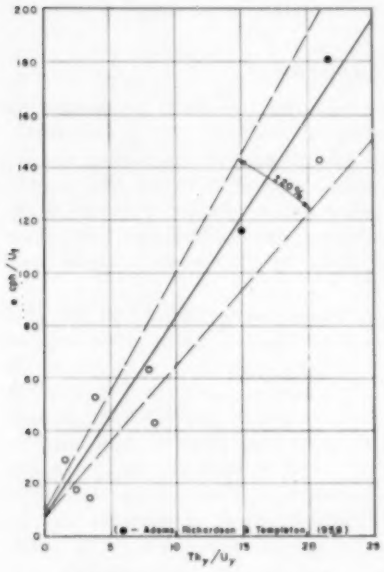

Figure 2. α cph/U_f versus Th_γ/U_γ

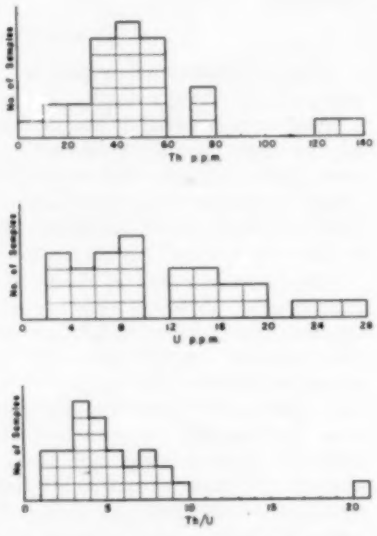

Figure 3. Th and U data on bauxites.

few samples were analyzed by this method and the data obtained (Table II) are shown in Figure 2, a plot of (alpha counts per hour/fluorometric uranium) against the gamma ray thorium-to-uranium (Th/U) ratio.

Figure 2 contains too few data to lend itself to a definite interpretation, but it appears that the relationship

$$\frac{\text{alpha cph}}{U_f} = K_1 + K_2\left(\frac{Th_\gamma}{U_\gamma}\right)$$

for bauxites may have a smaller K_2 value than that determined by Adams, Richardson and Templeton for a group of sediments composed predominantly

of limestones and shales. The diagonal line drawn on Figure 2 is taken from Adams et al. and represents the above relationship with values of 7.80 and 7.57 for K_1 and K_2, respectively.

The departure of the fluorometrically determined uranium values from the gamma ray values for samples KR-10, KR-38 and KR-80 might be attributed to lack of sample homogeneity, to absence of radioactive equilibrium, or, for samples KR-10 and KR-38, to incomplete extraction of the uranium in the chemical analysis. Because the thorium and uranium in a number of bauxites have been shown to be in equilibrium with their daughter elements, this paper continues on the assumption that this condition exists for all of the bauxites studied.

RESULTS AND DISCUSSION

Distribution of Thorium and Uranium in Bauxites.—The thorium and uranium analyses of 29 bauxite samples are given in Table II. The bauxites are divided into four groups on the basis of the type of rock from which they were derived; the parent rock types are acid igneous, basic igneous, shale, and limestone. Average thorium and uranium contents for each of the bauxite groups are shown in Table III, with averages for the parent materials taken from the literature.

In some cases there is doubt regarding the exact type of rock from which the bauxite is derived. The location of the Brazilian sample, for instance, is known only by the country. This bauxite may be derived from any of a number of acidic or metamorphic rocks (Table I), depending on which specific deposit was its source. The parents of other South American samples are also questionable. Discussions by Goldich and Bergquist and Hill indicate some uncertainty regarding a purely limestone parent rock for the Caribbean ores.

In grouping the bauxite samples the following relationships were considered: (i) the Caribbean and European bauxites, and the Missouri diaspore clay have limestone parent rocks; (ii) the Georgia and Mississippi samples are derived from shales, and included with them is the Bintan sample whose parent is a low grade metamorphic hornfels; (iii) basic igneous rocks are the parents of the bauxite samples from the Gold Coast, British Guiana, India, Palau Islands, Oregon, U.S.A., and Antrim, Ireland; (iv) acid igneous rocks, mainly nepheline syenites, are parents of the samples from French Guinea, Brazil, Surinam and Arkansas, U.S.A.

It is evident from the data in Tables II and III, not only that the thorium and uranium contents of bauxites are generally much greater than the average for crustal rocks, but also that there is a definite relationship between the thorium and uranium contents of a bauxite and its parent rock type.

For the 29 bauxite samples the thorium concentration ranges from 5.0 to 131. ppm and has an average value of 48.9 ppm; the uranium ranges from 2.7 to 26.7 ppm and has an average value of 11.4 ppm. The Th/U ratio ranges from 1.5 to 20.9 with an average value of 5.1 (Fig. 3).

The higher concentration of thorium and uranium in acid igneous rocks

Table II. Thorium and Uranium Determinations on Bauxites

Parent Rock	Sample	ppm Th	ppm U	Th/U	U_f ppm	α cph*	α cph / U_f
Carbonate							
	KR-3	31.5	9.6	3.3		285	
	KR-3B	34.8	8.1	4.3		194	
	KR-4	43.7	18.6	2.3	17.5	306	17.5
	KR-4B	42.0	17.0	2.5		264	
	KR-5L	46.5	26.7	1.7		346	
	KR-11L	47.3	6.5	7.3		265	
	KR-12L	43.8	8.4	5.2		243	
	KR-13L	51.5	8.3	6.2		280	
	KR-14L	55.6	12.4	4.5		265	
	KR-15L	59.2	7.5	7.9		306	
	KR-23L	56.0	13.0	4.3		361	
	KR-80	32.1	9.3	3.4	17.7	255	14.4
	KR-83	39.4	23.4	1.7		427	
Shale							
	KR-9L	58.7	7.1	8.3	7.1	305	43.0
	KR-17L	46.9	13.5	3.5		321	
	KR-18	34.6	15.4	2.2		239	
	KR-22	36.3	5.9	6.2		179	
Basic Igneous							
	KR-2L	21.2	2.7	7.9	2.9	176	60.7
	KR-7L	40.2	5.0	8.0		247	
	KR-8L	23.2	6.5	3.6		215	
	KR-10	5.0	3.3	1.5	0.4	12	30.0
	KR-20L	19.3	4.5	4.3		138	
	KR-84	15.1	2.9	5.2		114	
Acid Igneous							
	KR-1	127.4	24.1	5.3		1253	
	KR-6L	54.3	15.7	3.5		419	
	KR-26	72.0	17.0	4.2		520	
	KR-27	130.7	14.4	9.1		405	
	KR-31	74.2	3.6	20.6	3.1	442	142.6
	KR-38	75.8	19.8	3.8	6.6	348	52.7
Average (29 samples)		48.9	11.4	5.1			

* For sample surface of 20.3 cm^2

Table III. Average Values for Thorium, Uranium and Th/U Ratios in Bauxites and Parent Rocks

Rock Type	ppm Th	ppm U	Th/U
Carbonate rocks*	1.1	1.3	0.9
Concentration factor	(40.8)	(9.9)	(4.7)
Bauxites derived from carbonates (13 samples)	44.9	12.9	4.2
Uranium leached		(76%)	
Shales**	12.0	3.7	3.8
Concentration factor	(3.7)	(2.8)	(1.3)
Bauxites derived from shales (4 samples)	44.1	10.5	5.1
Uranium leached		(23%)	
Basic Igneous*	3.9	0.96	4.0
Concentration factor	(5.3)	(4.4)	(1.3)
Bauxites derived from basic igneous rocks (6 samples)	20.7	4.2	5.2
Uranium leached		(18%)	
Acid Igneous*	13.0	3.0	5.0
Concentration factor	(6.9)	(5.3)	(1.6)
Bauxites derived from acid igneous rocks (6 samples)	89.1	15.8	7.8
Uranium leached		(24%)	

* Evans and Goodman (1941)
** Adams and Weaver (1958)

as compared with basic igneous rocks is reflected by the bauxites derived from them. The bauxites with acidic parents are approximately four times richer in these elements than bauxites with basic parents. Bauxites derived from shales and carbonates are quite similar in both thorium and uranium content and are intermediate between the other two groups. The comparable radioactivities of the shale and limestone derivatives is not surprising if one considers, as Hartman suggested for Jamaican bauxite, that the source of the residual lateritic material is the clay impurity in the limestone.

It is noted from the data in Table II that the group of bauxites derived from carbonate rocks has the lowest Th/U ratio, and those derived from acid igneous rocks have the highest ratio. The low ratio for bauxites with limestone parent rocks is particularly well exhibited by the Caribbean samples, none of whose Th/U ratios is greater than 4.3.

Shown in Table III are average concentration factors for thorium and uranium during the formation of bauxite from the various types of source rock. The magnitude of these factors is dependent on two quantities: the fraction of the original rock mass removed in solution, and the amount of thorium and uranium leached. Assuming the thorium remains fixed, then the minimum concentration factor for this element depends only on the amount of parent rock removed. In the alteration of limestone to bauxite the thorium concentration is greatest, averaging 40-fold, while the alteration of shale results in less than 4-fold concentration of the thorium. As pointed out by Adams and Weaver, if all the thorium and uranium occurred in resistate minerals, lateritic weathering would concentrate both elements without changing the Th/U ratio. For each of the four groups of bauxites, the ratio is higher than the average for the parent rock type. Using the assumption that no thorium is lost, the concentration factor for this element multiplied by the uranium concentration of the parent rock gives the uranium concentration that the bauxite would have if no uranium were removed during bauxite formation. From such calculations it is estimated that approximately 20 percent of the uranium is leached from the igneous and shale parent rocks, and 75 percent from the carbonate rocks during lateritization. This is in close agreement with Adams and Weaver's report that an average of 80 percent of the uranium in a carbonate rock can be brought into solution by dissolving in weak acid.

From the foregoing considerations, and the rather general data in Table III, the following conclusions are drawn. In bauxites whose parent rocks are carbonates, the uranium retained is only the portion that occurred in the resistant minerals of the carbonate rock. Such a conclusion may also be valid for bauxites derived from shales and igneous rocks, in which case 70 to 80 percent of the uranium in shales and igneous rocks may occur either in primary or secondary resistate minerals. Because the Th/U ratio increases during bauxite formation, perhaps more of the thorium than of the uranium occurs in primary or secondary resistate minerals.

The reliability of the assumption that thorium is relatively immobile is demonstrated by the low Th/U ratio found in stream and ocean waters. Adams, Osmond and Rogers give a value of less than 0.01 for this ratio.

Table IV. Thorium and Uranium Contents of Some Bauxites and Their Parent Rocks

Sample	Location	ppm Th	ppm U	Th/U
KR-55, Nepheline syenite	Bauxite, Arkansas (Drill Core Samples)	19.3	4.9	3.9
Average of 5 bauxites		52.0	6.2	8.4
KR-81, limestone	Jamaica	(~ 0.2)*	1.3	< 0.2
KR-80, bauxite		32.1	9.5	3.4
KR-88, basalt	Antrim, N. Ireland	(~ 0.5)*	(<0.2)*	(4.0)**
KR-84, bauxite		15.1	2.9	5.2

* Error approaches 100% for such low level measurements
** Probable value (see Adams, Osmond, Rogers, 1959)

Table V. Thorium and Uranium in Arkansas Bauxite and Nepheline Syenite Samples

Location*	Sample	Description	ppm Th	ppm U	Th/U
Section 17	KR-54	Top of transported bauxite deposit	65.9	15.7	4.2
Section 16	KR-55	Fresh nepheline syenite	19.3	4.9	3.7
	KR-56	Weathered nepheline syenite	45.9	9.4	4.9
	KR-59	Limonite band between KR-56 and KR-57	36.9	2.3	16.1
	KR-57	Weathered; kaolinitic syenite	49.4	10.9	4.6
	KR-60	Clay layer between weathered syenite and bauxite	33.9	7.9	4.3
	KR-58	Near bottom of bauxite (pisolitic)	51.8	3.5	14.8
	KR-62	10 ft. horizontally from KR-58	34.0	10.3	3.3
	KR-63	10 ft. horizontally from KR-62	57.1	6.5	8.8
	$KR\text{-}61_1$	Near top of bauxite, 7 ft. above KR-58	50.5	3.9	13.0
	$KR\text{-}61_2$	Same horizon as $KR\text{-}61_1$	66.8	7.0	9.6
Section 26	KR-64	Granitic textured bauxite	77.5	24.9	3.1
	KR-65	Clay veinlets in bauxite	36.9	4.4	8.4
	KR-66	Pisolitic bauxite overlying KR-64	106.3	21.4	5.0

* Township 2 South, Range 14 West, Saline County, Arkansas

Comparison of the Thorium and Uranium Contents of some Bauxites with their Parent Rocks.—Table IV gives thorium and uranium data for bauxite samples from Arkansas, Jamaica and Northern Ireland, and for samples of their parent rocks, nepheline syenite, limestone and basalt, respectively, taken from the same areas as the bauxite samples. The Arkansas samples are taken from a drill core discussed in detail below. The nepheline syenite sample is somewhat kaolinized. The samples of Jamaican and Irish parent rocks are fresh.

Regarding the Arkansas samples in Table IV, the nepheline syenite is rather richer in thorium and uranium than the average acid igneous rocks; the bauxite contains less than the average amounts given in Table III for similar bauxites. The actual thorium and uranium concentrations of individual samples may not be highly significant, for it is shown later that the concentrations vary considerably within this deposit. Furthermore, the nepheline syenite, KR-55, is not quite fresh, and its thorium and uranium concentrations and the Th/U ratio may be greater than the unaltered rock.

The Jamaican parent rock contains an average amount of uranium for a limestone, but very little thorium. The typically low Th/U ratio of the limestone is reflected by the low ratio, 3.4, in the bauxite, KR-80. The thorium and uranium concentrations in KR-80 are close to the averages in Table III. Hartman estimated that 667 tons of the White limestone would be required to produce one ton of bauxite of 50 percent Al_2O_3. Using this estimate, and assuming no thorium is lost during alteration, a thorium concentration of 0.048 ppm in the limestone would result in the observed concentration of 32.1 ppm in KR-80, the bauxite. The thorium content of the limestone sample, KR-81, determined by gamma ray spectrometry is 0.19 ppm. This concentration is close to the limit of sensitivity of the spectrometer and is subject to large error. It is reasonable to conclude from the thorium measurements that the White limestone could well be the parent rock of the Jamaican bauxite.

The sample of basalt from Ireland is extremely low in thorium and uranium. The thorium and uranium contents of the bauxite derived from the basalt are also low compared to the average in Table III, but the Th/U ratio for the bauxite sample, KR-84, is 5.2. This is the same as the average Th/U ratio for bauxites derived from basic rocks.

Thorium and Uranium in Arkansas Bauxite.—Thorium and uranium data for the weathering sequence and drill core samples from Arkansas are presented in Tables V and VI, respectively. All of these samples, with the exception of KR-54, are taken from residual deposits of bauxite that overlie the parent syenite. KR-54, like KR-26 in Table II, is from a plastic or colluvial type of deposit which overlies the Midway clays. KR-54 is taken from the top of a transported bauxite deposit, just below the contact with sediments of the Wilcox Group.

The two transported bauxite samples, KR-26 and KR-54, have very similar thorium, uranium and Th/U values, but these values are not distinctively different from the analyses of the many residual bauxite samples. It is thought (Shepard, pers. comm.) that as a result of transportation of

Table VI. Thorium and Uranium in Drill Core Samples of Arkansas Bauxite

Sample	Footage	ppm Th	ppm U	Th/U	Lithology
KR-67	136-138	24.5	5.4	4.5	Dark brown, sandy carbonaceous clay
KR-68	138-140	71.8	6.6	10.9	Brown, carbonaceous clay, and gray, fragmental, pisolitic bauxite
KR-69	140-142	94.8	8.3	11.4	Pink and gray, fragmental, pisolitic bauxite
KR-70	142-144	87.5	8.4	10.4	Red and gray, fragmental, pisolitic bauxite
KR-71	144-146	85.3	8.6	9.9	Red and gray, pisolitic, fragmental, slightly sideritic bauxite
KR-72	146-148	91.8	8.6	10.7	Red with some pink, pisolitic, fragmental, slightly sideritic bauxite
KR-73	148-150	88.1	8.1	10.9	Red and gray, pisolitic, slightly sideritic bauxite
KR-74	150-152	94.7	7.8	12.2	Gray with some red, pisolitic, slightly sideritic bauxite
KR-75	152-154	90.4	7.1	12.7	Same as above
KR-76	154-156	87.3	6.9	12.6	Same as above
KR-77	156-158	73.6	8.8	8.3	Same as above, with occasional kaolinitic flecks
KR-78	158-160	51.6	7.2	7.1	Gray bauxite and siderritic clay with kaolin fragments
KR-79	160-163	24.7	4.8	5.2	Gray with some pink, kaolinitic, slightly siderritic, weathered syenite

Table VII. Thorium and Uranium in Material Balance Samples

Weight lbs.	Surinam	ppm Th	ppm U	Th/U	U_f	Th_c	alpha* cph	% Th	% U
1.9	bauxite	74.2	3.6	20.9	3.1		342		
1.0	calcined alumina	4.9	0.3	14.7			1.1	3.5	5
0.48	fine red mud	261	11.6	24.2		249	1332	96	82
0.05	classifier sand	122	10.1	11.9			629	4.3	7.4
								103.8%	94.4%
	Arkansas								
2.25	bauxite	75.8	19.8	3.8	6.8		346		
1.0	calcined alumina						0.8		
1.04	fine red mud	120	39.8	2.8			750	73	93
0.22	classifier sand	70.1	6.4	11.0			318	9.1	3.1
								82%	96%

* For sample surface of 20.3 cm^2

the bauxite these samples have a smaller accessory mineral content. This hypothesized decrease of accessory minerals does not noticeably affect the amounts of thorium and uranium found in the bauxite. The radioactive elements must, then, be transported either in extremely fine grained primary resistate minerals or in resistate hydrolyzate minerals.

The *Weathering Sequence* samples were collected in Tp. 2 S., R. 14 W., Sect. 16 and 26, of Saline County, Arkansas. Figure 4 is a diagrammatic section showing the relative locations of the samples taken from the Section 16 mine. From the analyses of these samples the following observations are made:

i) The thorium and uranium concentrations increase by a factor of 2 to 3, in the distance of a foot or so from the relatively fresh nepheline syenite to the weathered, kaolinitic syenite.

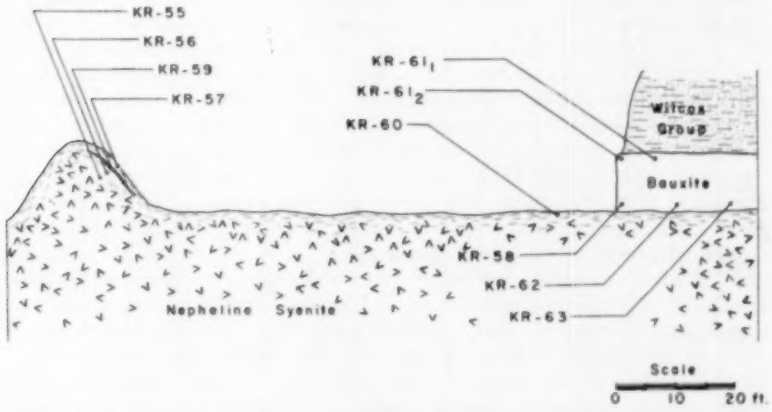

Figure 4. Diagrammatic section showing relative locations of Arkansas samples.

ii) The thin limonite band in the kaolinitic rock and the clay material between the nepheline syenite and the overlying bauxite contain less thorium and uranium than the material immediately above or below. The hard limonite band, about ½ inch thick, is similar to that described by Goldman. If the uranium in bauxites occurred as ions adsorbed on the ferric hydroxide, the limonitic band that is represented by sample KR-59 might be expected to contain more than the measured 2.3 ppm uranium. The low radioactivity of the clay, sample KR-60, is in agreement with Frederickson's total activity measurements.

iii) The variations between samples KR-58, KR-62 and KR-63, and also between KR-61$_1$ and KR-61$_2$ illustrate large changes in thorium and uranium concentrations that occur in the distance of a few feet, with no apparent change in bauxite texture or vertical position in the deposit.

iv) Samples KR-64 and KR-66 from the Section 26 mine have higher

radioactivity than the samples from Section 16 mine. The pisolitic bauxite (KR-66) contains more thorium than the underlying bauxite with granitic texture (KR-64), but the uranium contents of the two samples are approximately the same. The clay veinlets in these bauxites, as described by Goldman and Tracey, are much less radioactive than the bauxite, comparable to the clay layer of which KR-60 is a sample.

The *Drill Core* samples were taken from a hole drilled in the NE ¼, SE ¼, Sect. 26, Tp. 2 S., R. 14 W., Saline County. The 27-foot section of core includes 18 feet of pisolitic bauxite that grades into 4 feet of dark brown sandy and carbonaceous clay at the top of the section, and into 5 feet of kaolinitic clay and weathered nepheline syenite at the bottom. The lower

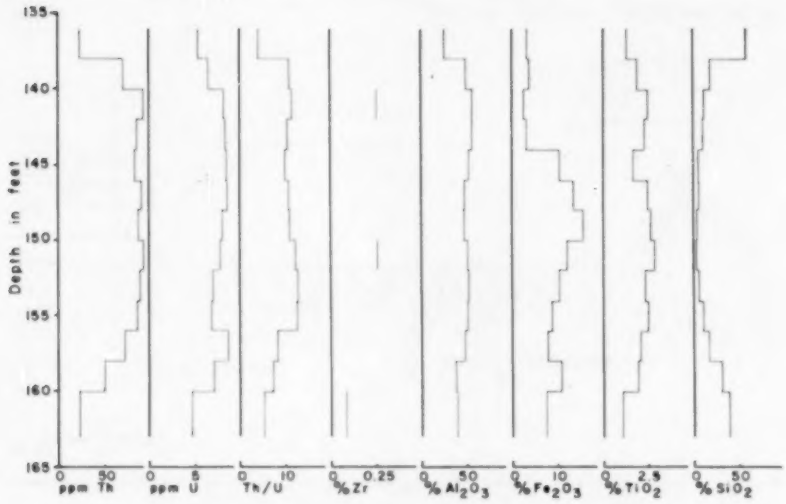

Figure 5. Analyses of Arkansas drill core.

half of the bauxite is predominantly gray in color, the upper half predominantly red. Each sample listed in Table VI represents a 2-foot section of the core except KR-79 which represents the bottom 3 feet. Figure 5 illustrates results of the routine analyses for iron, aluminum, titanium and silica made by the Aluminum Company of America, as well as the thorium, uranium, and zirconium determinations on the drill core samples.

It is seen from Table VI that the thorium and uranium concentrations, as well as the Th/U ratio, increase rapidly from the nepheline syenite to the bottom of the bauxite, remain fairly constant through the bauxite section, and decrease in the top, carbonaceous part of the core.

From the nepheline syenite to the bauxite the uranium concentration does not quite double, but the thorium concentration is almost quadrupled. The

drop in uranium concentration from KR-77 to KR-76, although it is close to the limits of error, is considered real. Figure 5 shows a similar drop in the Fe_2O_3 concentration from sample KR-78 to KR-77. It is suggested that the decrease in uranium content may be related to a change from a true residual deposit to overlying transported material. Another possibility is that corrosion of resistates, for example zircon, has permitted the leaching of more uranium from this level.

The nine samples representing the bauxite portion of the drill core contain an average of 88.2 ppm of thorium, 8.1 ppm of uranium, and have an average Th/U ratio of 11.0.

The histograms in Figure 5 indicate that concentrations and depletions similar to those observed for uranium and thorium occur for alumina, ferric oxide and titania, whereas silica behaves inversely. Three analyses for zirconium show more than a 5-fold increase from the nepheline syenite to the bauxite with apparently little change in concentration through the bauxite.

For the decreased concentrations of aluminum and ferric hydroxides, and the increased concentration of silica, at the top of the drill core there are two possible explanations that suggest different modes of thorium and uranium occurrence in the bauxite. If the lateritic materials are leached from the top of the section by the influence of organic matter, the increased silica concentration in KR-67 and KR-68 should be accompanied by an increase of resistate accessory minerals. The decrease in thorium and uranium concentrations at the top of the drill core would then indicate that these elements had been held by the hydrolyzate minerals. On the other hand, if the composition of the top of the section is the result of dilution by quartzitic alluvial material, the radioactive elements may occur in resistate minerals. The approach of the Th/U ratio at the top of the section to a value typical of common crustal material is perhaps a factor favoring the latter explanation.

Concentration of Thorium and Uranium During the Processing of Bauxite.—Material balance samples from the St. Louis plant, which treats Surinam bauxite, and the Bauxite Alumina Works, which treats Arkansas ore, were studied. These samples, representing seven days' operation of each of the plants, are comprised of bauxite, calcined alumina, fine red mud, and classifier sand. The classifier sand is the coarser fraction of this mud, which is removed from the mud thickeners to reduce the load. The classification of the red mud and the coarse sand is not perfect; a fine sand fraction remains in the red mud. These samples were obtained through the courtesy of the Aluminum Company of America.

The analytical results of the material balance study are presented in Table VII. Column 1 gives the weight of bauxite required and the weights of mud and sand obtained in producing 1 lb. of calcined alumina. Gamma ray data are shown for all of the Surinam samples, but the Arkansas alumina sample, having an alpha activity of only 0.8 cph, was not amenable to gamma ray spectrometry. The uranium content of the Surinam bauxite, and the thorium content of the Surinam red mud were also measured independently by chemical methods that gave good agreement with the spectral analyses. Fluorometric uranium determinations for the Arkansas bauxite gave markedly

lower values than the gamma ray method. This may have been the result of incomplete extraction of the uranium in the fluorometric procedure. Such a problem was encountered with the sample of Arkansas bauxite cited by Adams, Richardson and Templeton, but the radioactive decay series were shown to be in equilibrium in that sample.

The samples of calcined alumina produced from both Surinam and Arkansas bauxites have very low radioactivities. Most of the thorium and uranium introduced in the feed bauxite is concentrated in the waste products of the Bayer process: the red mud and the classifier sand. The red mud makes up 80 to 90 percent of the waste material, and it contains much more of the thorium and uranium than the classifier sand. The red mud from the Surinam bauxite treatment plant contains 281 ppm of thorium and 11.6 ppm of uranium; this is 96 percent of the thorium and 82 percent of the uranium that was originally contained in the bauxite. The red mud from the Arkansas bauxite treatment plant contains 120 ppm of thorium and 39.8 ppm of uranium; this represents 73 percent of the thorium and 93 percent of the uranium from the feed bauxite.

The concentrations of uranium in the red mud and coarse sand samples of the Surinam material balance are essentially the same, but the Th/U ratio is 24.2 in the mud and 11.9 in the sand. This indicates that in the Surinam bauxite the modes of occurrence of thorium and uranium may be different, with the thorium occurring in finer grained particles than the uranium. In the Arkansas material balance the Th/U ratio of the red mud is much less than the Th/U ratio of the classifier sand.

Samples elutriated from Surinam and Arkansas red muds, consisting of the less than 6 micron size fraction, were alpha counted. The measured activities, 1215 and 1040 counts per hour, respectively, are not greatly changed from the activities of the whole red mud samples. Thus, the alpha emitting nuclides can be retained in very fine grained material.

A portion of the less than 6 micron Surinam sample was leached with hydrochloric acid. Much of the iron was removed, and the sample weight was reduced by approximately 70 percent. The measured alpha activity of the residue was 1,480 counts per hour, and the calcined leach, whose mass is approximately twice that of the residue, had an alpha activity of 1,230 counts per hour.

Without distinguishing parent from daughter elements, or thorium from uranium series, the results of the leaching experiment show that roughly 1/3 of the alpha emitters resist severe leaching, and remain in the residue of the red mud. The retention of these elements suggests that they are held in resistate minerals. It is also possible that some of the radioactive material in the leach was removed from resistates. A further indication that thorium occurs in resistate minerals is the fact that this element is in equilibrium with its daughters in the Surinam red mud sample (Table VII). The existence of radioactive equilibrium in this sample would be extremely unlikely, unless the entire radioactive decay series were within a closed system, i.e. within resistate mineral grains.

X-ray diffraction analysis of the leached red mud residue showed this

Table VIII. Zirconium in Bauxites

Sample		Zirconium % by wt.
Bauxites derived from carbonate rocks		
KR-3		0.05
KR-3B		0.049
KR-4		0.05
KR-4B		0.053
KR-5L		0.022
KR-11L		0.040
KR-12L		0.049
KR-13L		0.062
KR-14L		0.061
KR-15L		0.048
KR-23L		0.049
	Average	0.048
Bauxites derived from shales		
KR-9L		0.022
KR-17L		0.044
KR-18		0.10
KR-22		0.07
	Average	0.059
Bauxites derived from basic igneous rocks		
KR-2L		0.030
KR-7L		0.132
KR-8L		0.108
KR-10		0.02
KR-20L		0.057
	Average	0.069
Bauxites derived from acid igneous rocks		
KR-1		0.65
KR-6L		0.153
KR-26		0.076
KR-27		0.242
KR-31		0.126
	Average	0.248
Arkansas samples		
KR-55	relatively fresh nepheline syenite	0.055
KR-56		0.064
KR-57	kaolinized nepheline syenite	0.103
KR-79	drill core syenite	0.085
KR-74	drill core bauxite	0.257
KR-69	drill core bauxite	0.253
Treatment plant samples		
Surinam bauxite		
KR-34	calcined alumina	0.01
KR-33	classifier sand	0.112
KR-28	classifier sand	0.078
KR-32	red mud	0.346
KR-24	red mud (-6 micron)	0.174
Arkansas Bauxite		
KR-29	classifier sand	0.460
KR-30	red mud (-6 micron)	0.462

material to consist mainly of anatase, with rutile, quartz, and possibly gypsum and gibbsite in minor accounts.

The small amounts of thorium and uranium present in samples of calcined alumina (Table VII) indicate that similar low radioactivity should be

characteristic of reduced aluminum metal. A number of aluminum metal samples discussed by Adams and Richardson had alpha counting rates only slightly above background.

Zirconium in Bauxites.—Because of the chemical similarities between thorium, uranium and zirconium many of the bauxite and associated samples were analyzed for this element. Table VIII gives zirconium determinations for 25 bauxite samples, 6 bauxite and nepheline syenite samples from Arkansas, and 7 samples from bauxite treatment plants.

The concentration of zirconium in bauxite appears to be related to the type of rock from which the bauxite is derived. A histogram of the distribution of zirconium concentrations, Figure 6, illustrates this relationship. The zirconium contents of bauxites derived from carbonates are uniformly low, ranging from 0.022 to 0.062 percent and averaging 0.048 percent. Bauxites derived from shales and basic igneous rocks have a wider range

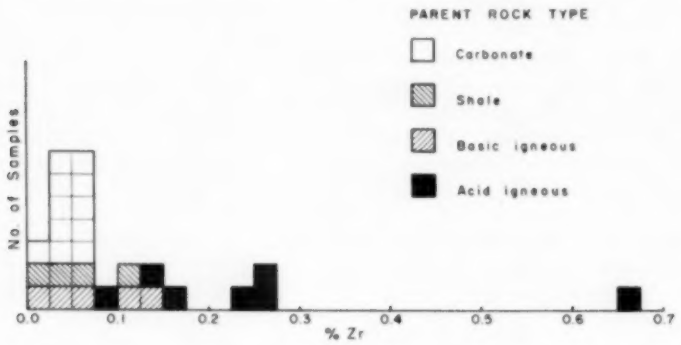

Figure 6. Zirconium data on bauxites.

of zirconium concentrations, with average values of 0.059 and 0.069 percent, respectively. Bauxite daughters of acid igneous rocks have zirconium contents ranging from 0.076 to 0.65 percent, and averaging 0.248 percent. The relative zirconium concentrations in the 4 groups of bauxites compare closely with the relative zirconium concentrations quoted by Degenhardt for each of the 4 types of parent rocks.

There appears to be no relationship between the zirconium contents of bauxites and the thorium or uranium contents. A positive relationship between these elements might be expected if thorium and uranium were present in zirconium minerals. Degenhardt refers to the corrosion of zircons in laterites, and Frederickson states that portions of the bauxite drill core that he studied showed high assays for zirconium and contained no zirconium minerals. With these considerations, the absence of a correlation between thorium or uranium content and zirconium content in bauxites is not improbable.

Colorimetric zirconium determinations on Arkansas samples show a concentration of 0.055 percent Zr in the freshest nepheline syenite sample, increasing to 0.103 percent Zr in the weathered syenite, and reaching 0.257 percent Zr in the bauxite. This compares favorably with Gordon and Murata's spectrographic determination of 0.050 percent Zr in the nepheline

TABLE IX

POTASSIUM IN BAUXITES

Sample	Description, Location	% K
KR-1	Bauxite, French Guinea	0.03
KR-2L	Bauxite, Gold Coast	0.07
KR-3	Bauxite, Dominican Republic	0.29
KR-3B	Bauxite, Dominican Republic	0.04
KR-4	Bauxite, Jamaica	−0.05
KR-4B	Bauxite, Jamaica	0.24
KR-5L	Bauxite, Jamaica	0.15
KR-6L	Bauxite, Brazil	0.27
KR-7L	Bauxite, British Guiana	0.21
KR-8L	Bauxite, India	0.14
KR-9L	Bauxite, Bintan, East Indies	0.12
KR-10	Bauxite, Palau Islands	0.04
KR-11L	Bauxite, Istria, Yugoslavia	0.13
KR-12L	Bauxite, Dalmatia, Yugoslavia	0.3
KR-13L	Bauxite, Italy	0.21
KR-14L	Bauxite, France	0.08
KR-15L	Bauxite, Greece	0.30
KR-17L	Bauxite, Henry, Georgia	0.22
KR-18	Low grade bauxite, Georgia	0.24
KR-20L	Composite sample, Oregon	0.12
KR-22	Low grade bauxite, Mississippi	0.19
KR-23L	Diaspore Clay, Missouri	1.3
KR-26	Bauxite, Surinam	0.21
KR-27	Bauxite, Arkansas	0.41
KR-31	Bauxite, Surinam material balance	0.15
KR-32	Red mud, Surinam material balance	0.60
KR-33	Classifier sand, material balance	−0.04
KR-34	Calcined alumina, Surinam material balance	−0.22
KR-37	Red mud, Arkansas material balance	0.21
KR-38	Bauxite, Arkansas material balance	−0.10
KR-55	Nepheline syenite, Arkansas	5.62
KR-64	Granitic textured bauxite, Arkansas	0.02
KR-67	Carbonaceous clay, Arkansas drill core	0.21
KR-68	Clay and bauxite, Arkansas drill core	0.03
KR-76	Bauxite, Arkansas drill core	0.09
KR-79	Nepheline syenite, Arkansas drill core	2.11
KR-83	Bauxite, Jamaica	0.3

From the size of the negative values and other considerations, the estimated error in these measurements is less than 0.1 percent K.

syenite, but is double their value of 0.13 percent Zr in the bauxite. Degenhardt gives values averaging 0.071 percent Zr for nepheline syenites, and 0.051 percent Zr for European bauxites derived from limestones.

The Surinam material balance samples show that approximately 75 percent of the zirconium in the bauxite is concentrated in the red mud. The zirconium concentration increases from 0.126 percent in the bauxite (KR-31) to 0.346 percent in the red mud. Zirconium is present in the calcined alumina in an extremely low concentration. Because the concentration of zirconium in the classifier sand and in the less than 6 micron fraction is lower than in the red mud, zirconium must occur in an intermediate grain size fraction. In contrast to the Surinam samples, the Arkansas classifier sand and less than 6 micron fraction of the red mud contain equally high zirconium concentration, 0.46 percent. This suggests a more uniform distribution of zirconium in all grain sizes in the Arkansas bauxite.

ECONOMIC CONSIDERATIONS

The relatively high concentration of thorium and uranium in bauxites presents a convenient radiometric method of prospecting for this ore.

Although more detailed work would be required on individual bauxite deposits, it is suggested that a usable relationship between the radioactivity and the grade of the ore might favor the substitution of a field radiometric technique for some of the drilling and laboratory analyses now used in bauxite mining operations.

Another economic consideration is that of recovering thorium as a by-product of the alumina process. The concentration of 281 ppm of thorium in the red mud of the East St. Louis alumina plant indicates that for each ton of alumina produced, $\frac{1}{4}$ lb of thorium is concentrated in approximately $\frac{1}{2}$ ton of red mud. This alumina plant alone, having an annual capacity of more than 300,000 short tons, might produce 40,000 lbs of thorium per year, assuming 50 percent recovery.

SUMMARY AND CONCLUSIONS

The principal conclusions of this study are:

1. Bauxites generally contain concentrations of thorium and uranium greater than the earth's crustal average.
2. A relationship exists between the type of rock from which a bauxite is derived and the thorium, uranium and zirconium contents of the bauxite.
3. There are a number of indications that thorium and uranium are held in either primary or secondary resistate minerals in bauxites.
4. In the process of extracting alumina from bauxite, over 70 percent of the thorium and uranium are concentrated in the red mud. The alumina and aluminum metal contain very small amounts of these elements.

ACKNOWLEDGMENTS

This investigation was generously supported through Grant C-0009 from the Robert A. Welch Foundation. The authors wish to acknowledge the

cooperation of the Aluminum Company of America, Ltd., in contributing many of the bauxite samples studied, and assisting in the collection of samples on their Arkansas properties. The help of Dr. H. Hoss, Dr. R. Pliler and Miss M. C. Kline at The Rice Institute and of Dr. J. E. Richardson of Shell Development in obtaining some of the analyses given in this paper is also gratefully acknowledged.

THE RICE INSTITUTE,[1]
HOUSTON, TEXAS.
April 22, 1960

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Economic Geology
Vol. 55, 1960, pp. 1676–1707

SULFUR ISOTOPES AND THE ORIGIN OF THE SULFIDE DEPOSITS OF THE BATHURST–NEWCASTLE AREA OF NORTHERN NEW BRUNSWICK

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ABSTRACT

The regional geology of the Bathurst-Newcastle area is briefly outlined. There are two types of sulfide deposits in the area: (a) epigenetic fissure deposits, and (b) massive sulfide deposits. Geological evidence can be variously interpreted to suggest a syngenetic, a source bed, or a magmatic hydrothermal origin for the massive sulfide deposits.

S^{32}/S^{34} ratios are presented for more than three hundred sulfide samples from the host rocks and sulfide deposits. Four granite bodies are dated by the potassium-argon method. Model lead ages are presented for five galena samples.

Sulfides disseminated through the black shales and argillites of the host rocks are enriched in S^{32} (mean value 22.31) relative to the meteoritic ratio, and have a broad range of values.

S^{32}/S^{34} ratios for the sulfide deposits fall into two distinct groups. In general one group (21.88–22.05) represents the massive sulfide deposits, while the other group (22.18–22.21) represents the fissure deposits. This suggests two separate, but probably closely related sources for the sulfur.

Granites intrusive into the host rocks of the sulfide deposits have a mean age of 386 ± 10 m.y. Lead minerals in the sulfide deposits have a mean model lead age of 370 ± 20 m.y. Thus the lead minerals and the granite bodies were emplaced during the same major orogenic event.

The sulfide deposits of the Bathurst area have a narrow range of S^{32}/S^{34} values. Sulfide deposits thought to have a magmatic hydrothermal origin all have a narrow range of S^{32}/S^{34} values. It therefore seems reasonable that well homogenized magmatic hydrothermal solutions are the most logical source for the sulfide deposits.

The homogeneity of the lead isotope abundance data gives strong independent evidence that the ores are of a magmatic hydrothermal origin.

The problem of why the massive sulfide deposits are enriched in S^{34} is open for further investigation.

INTRODUCTION

THE principles of isotope fractionation are now fairly well understood. Therefore a measurement of the extent of isotopic fractionation that has occurred in any element should be indicative of the processes through which that particular element has gone. However, natural processes are commonly of a complicated character, and quantitative agreement between theory and observation may not be found.

Sulfur is of particular interest in regard to isotope abundance studies in view of its many forms and its wide distribution. The S^{34} content of sulfur in nature is known to vary by almost ten percent. As it is the principle non-metal in most ore deposits, an understanding of its behavior in geological processes should aid in the critical evaluation of the genesis of sulfide deposits.

Large massive sulfide bodies were discovered in the Bathurst area of northern New Brunswick in 1953. Since then, exploration and development work has advanced rapidly. To date, more than twenty large sulfide bodies have been located. Many are multi-million ton massive sulfide deposits. The geological environment of these deposits is complex and varied. As a result of these variations, hydrothermal, source bed, and syngenetic origins have been advocated for these deposits.

Late in 1957, sulfur isotope compositions were determined for a selected suite of sulfide samples from various geological environments in the Bathurst area (11). The results proved to be significant as well as interpretable, and indicated that a detailed study would be rewarding. In the detailed study that followed, sulfur isotope variations were determined within twenty-five sulfide deposits, and in the sulfides disseminated throughout the sedimentary host rocks, and intrusive granites. It was anticipated that relations within these environments would reflect the origin of the sulfide deposits. In addition it was hoped that important statistical and geochemical data on variations within these environments would be forthcoming.

Geologic ages have been determined by the potassium-argon method on

four granite bodies intrusive into the host rocks of the sulfide deposits. The Geophysics Department of the University of Toronto supplied revised lead isotope data on a suite of lead minerals from the area. This latter study was undertaken to determine whether there was any genetic relation between the granite intrusions and the lead minerals.

Here then is a detailed study of the isotopic variations of sulfur not only within a single deposit, but throughout several deposits and geologic environments in a complex geologic subprovince. Sufficient care in sampling

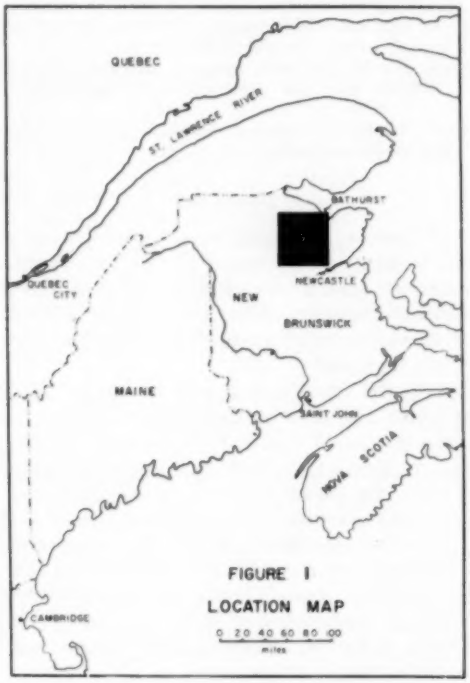

FIGURE 1
LOCATION MAP

and in analytical processing has been taken to insure the significance of the results. Over three hundred natural samples containing sulfur were subjected to isotopic analysis.

LOCATION AND ACCESSIBILITY

The Bathurst-Newcastle area is situated in the northeast corner of the Province of New Brunswick, Canada (Fig. 1). The towns of Bathurst and Newcastle are easily accessible by road and railway from all eastern points in Canada and the United States. Both towns possess natural harbors from which the shipping lanes of the North Atlantic and the St. Lawrence Seaway

are readily accessible. An excellent network of large navigatable rivers and well maintained lumber roads dissect the Bathurst-Newcastle area.

TECHNIQUES AND PROCEDURES

Sulfur Isotope Analysis.—The sulfide ores from the massive sulfide deposits of the Bathurst area are extremely fine grained. In order to obtain a monomineralic sample for analysis, considerable discrimination is necessary in the selection of the raw sample. When coarse grained and/or monomineralic samples were selected for analysis, the individual sulfides usually could be isolated by hand separation with the aid of a magnifying glass. In some instances, it was necessary to revert to heavy liquids, a shaking table, or to an isodynamic separator. After the individual sulfides were isolated, they were ground until all the sample passed through a 60 mesh screen. Generally 0.5 to 1.0 grams of the sample were prepared. All samples chosen for analysis were spatially distributed throughout the deposit.

The sulfides in the granites and sedimentary host rocks were concentrated by heavy liquids, and further cleaned on an isodynamic separator. Occasionally the latter step was not successful and the pyrite had to be concentrated by hand under a microscope.

The sulfate from mine waters was precipitated as barium sulfate, and heated with carbon to reduce it to barium sulfide. The barium sulfide was extracted in acidified cold water and the sulfur precipitated as lead sulfide.

In preparation for the isotopic analysis each sulfide specimen was converted to sulfur dioxide in the Laboratory of Economic Geology, Yale University, by a standard procedure described by Jensen (11, p. 376–377).

The Potassium-Argon Analysis.—The potassium-argon method of determining ages is based on the decay of potassium 40 to argon 40 (2). The argon content of the biotites were determined by isotopic dilution, using A^{36} as a measure of air contamination.

Two mass-spectrometers, located at the Massachusetts Institute of Technology, are used in the argon analysis. One is a Model 21-620 Consolidated Electrodynamics Corporation cycloidal focusing instrument. The other is a 60° sector, 6 in. radius, Nier type instrument. The two mass-spectrometers are connected directly to the gas purification train. The Model 620 instrument is used to measure the A^{38}/A^{40} ratio, while the Nier type instrument is used to measure the A^{36}/A^{38} ratio. Reproducibility of argon analysis in this type of material has been found to be normally better than two percent.

The potassium content of the biotites was determined on a Perkin-Elmer Model 146 flame photometer. This instrument utilizes lithium as an internal standard. Replicate analysis of the same solution on this instrument gives a standard deviation of approximately one percent. The following values for the decay constants of potassium were used in this work.

$$\lambda_e = 0.585 \times 10^{-10}\ \text{yr}^{-1}$$
$$\lambda_\beta = 5.30 \times 10^{-10}\ \text{yr}^{-1}$$
$$K^{40} = 1.22 \times 10^{-4}\ \text{g/gK}$$

GEOLOGY OF THE BATHURST-NEWCASTLE AREA NEW BRUNSWICK

The Province of New Brunswick can be divided into four basic geologic and physiographic divisions: the Southern Highlands, the Eastern Plain, the Central Highlands, and the Northern Upland.

The Bathurst area lies in the Central Highlands, which stretch southwest from Bathurst across the Province. The Highlands are underlain by a broad belt of Paleozoic sedimentary and volcanic rocks, which are cut by large granite batholiths of probable Devonian age. The Bathurst area lies just at or beyond the northeastern extension of these major batholiths. The area to be described lies between latitudes 47° 00′ and 47° 45′ north, and longitudes 65° 30′ and 66° 30′ west.

General Geology.—The geology of the area has been described by Smith and Skinner (26) and their map (Fig. 2, p. 151) reproduced here as Figure 2, shows the distribution of the rock formations in relation to the sulfide deposits.

Sulfide Deposits.—The sulfide deposits of the district are of two general types: (a) massive sulfide replacement deposits, and (b) small, coarse grained, fissure type deposits. The latter are confined mainly to an east-west fissure system associated with the Rocky Brook-Millstream break, or breaks parallel to it. These deposits commonly occur where north to northwest trending crossfaults cut the east-west system. They are fissure fillings, small replacement bodies along shears, or actually in shears. The mineralization of the fissure deposits is varied, and although considerable overlapping and gradation is present, the deposits may be sub-grouped on a mineralogical basis as follows: (a) quartz-arsenide, (b) quartz-chalcopyrite, (c) chalcopyrite-pyrrhotite, (d) sphalerite-chalcopyrite-pyrrhotite-galena-silver, and (e) galena-sphalerite-calcite-silver deposits. Though small, they fortunately are, as a rule, of better grade than the large replacement sulfide bodies. The grain size of these sulfides make them very amenable to concentration. The Nigadoo, Sturgeon River, Keymet and Beresford deposits, as well as numerous other small mineral occurrences, can be grouped under this type.

The massive sulfide replacement deposits can be further sub-divided into two types: (a) extremely fine-grained pyrite with galena, sphalerite, and silver, with minor pyrrhotite and chalcopyrite; (b) a pyrrhotite-chalcopyrite type with minor galena, sphalerite, and silver values. The two types are in places associated, and where this is the case, the pyrrhotite-chalcopyrite mineralization is thought to be the younger. Quartz and minor carbonate accompany the massive sulfide deposits.

Weathering and oxidation have produced striking gossan zones over some of the sulfide deposits. Complete oxidation to depths of thirty or forty feet is common. A few of the massive sulfide bodies have little or no gossan, whereas nearby masses are deeply oxidized. Secondary enrichment is present in some of the deposits and notably absent in others.

Each massive sulfide deposit has its own characteristic physical features that reflect its local geologic environment. Yet, all these deposits have many

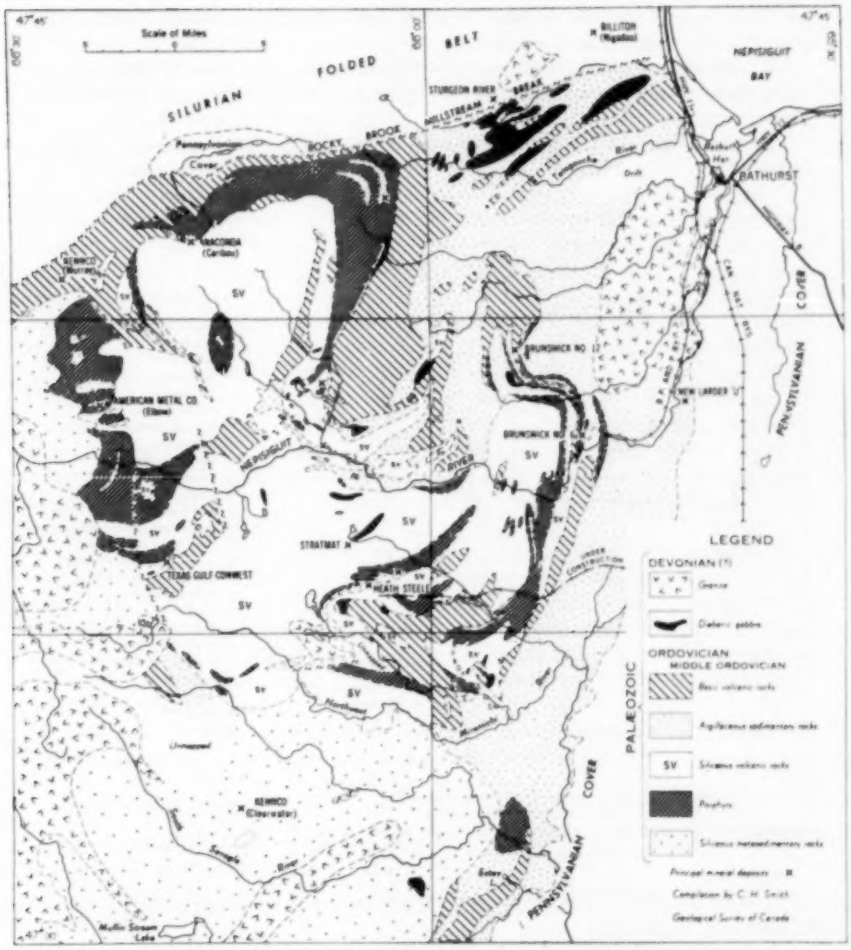

Figure 2.—Geology of the Bathurst-Newcastle district, New Brunswick.

features in common. The following generalizations can be made regarding the pattern of the deposits. Excluding the last item, these generalizations may be regarded as secondary ore controls.

1. Most deposits occur in the interlayered sedimentary-"porphyry"-volcanic complex surrounding the siliceous volcanic center.

2. The majority of the deposits are spatially related to porphyry-sedimentary contacts referred to locally as transition zones.

3. In most cases the sulfides replace the sedimentary member with little or no sulfide content in the porphyry.

4. Although the sulfides are not restricted to any one type of sedimentary rock, they commonly replace chloritic schists, iron formation, or ferruginous slates.

5. Many deposits are associated with drag-folds or other sharply plunging features.

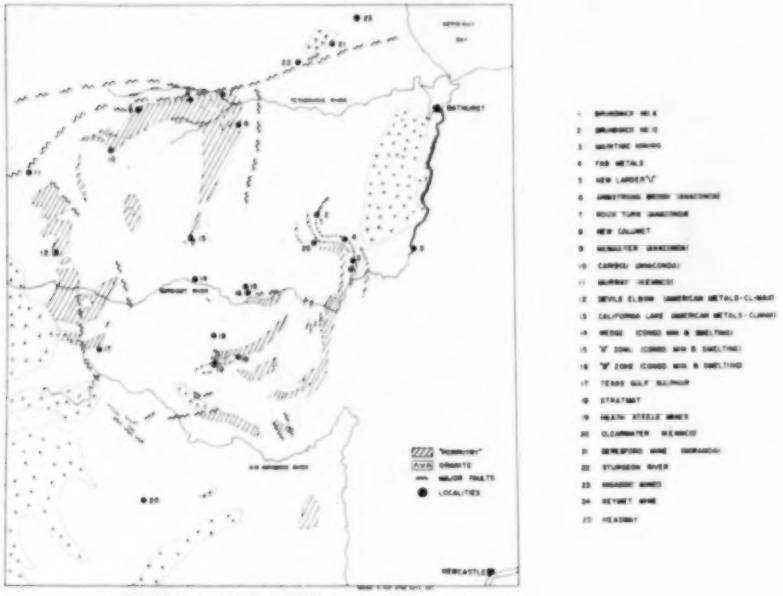

FIGURE 3 BATHURST - NEWCASTLE AREA
SHOWING THE DISTRIBUTION OF "PORPHYRY", GRANITE, AND SULFIDE BODIES

6. The transition zone appears to have been particularly subject to drag folding and shearing.

7. Sulfide samples from one deposit cannot be distinguished from those of another deposit. Mineralogical and textural features are strikingly consistent.

Possible variants from the geological environment of the "typical Bathurst type" are the New Larder "U", Clearwater and Stratmat 61 deposits. At Stratmat 61 a spatial relationship between the chloritic zone and a nearby gabbro is conceivable. The New Larder "U" and Clearwater deposits are found away from the main transition zone, and drag folding is not as pronounced as in the other deposits.

Origin of the Massive Sulfide Deposits.—The association of the sulfides with porphyry-sedimentary contacts is evident. The reasons for this are obscure, but special conditions must have existed to control the localization of massive sulfides along this geologically favorable zone.

The special conditions may have been one of the following:[1] (a) The relationships could be a genetic one, wherein the sulfides may be related to the actual processes of sedimentation. (b) The sulfides may be genetically related to processes of sedimentation but reconcentrated by metamorphism. (c) The sulfides may have been reconcentrated by metamorphism from the associated volcanics. (d) The control may be primarily a structural one, in which structural intersections have tapped reservoirs of conventional hydrothermal solutions and formed sulfide bodies in appropriate structural traps.

McAllister (19), and Smith and Skinner (26) seem to favor an origin genetically related to granite intrusions in the area. Sullivan (28) suggests that the metals have accumulated from tuffs during metamorphism. Knight (13) proposes that the sulfides were concentrated from a sedimentary horizon by a rise in temperature of the rock environment. Stanton (27) outlines the origin of these sulfides as formed by sulfate reduction in an "off-reef facies in seaboard volcanic areas." This would indicate a syngenetic origin. Stanton notes however, that there is very little evidence to denote whether metals other than iron "could have been localized and concentrated during sedimentation" or whether they were "derived from elsewhere and later precipitated by the iron sulfide."

Oftedahl, although not referring directly to the sulfide deposits of the Bathurst area, has outlined a somewhat similar origin for this type of deposit (20). He suggests that the "porphyry" is a waterlaid pyroclastic and that the sulfides have been deposited by submarine volcanic or hot spring activity. McAllister (18) suggests that the massive sulfide deposits are a facies of the iron formation. In short, a hydrothermal, a syngenetic, and a source bed origin all have been advocated.

Perhaps it would be well to outline the geologic relations suggestive of each of these modes of origin as found in the Bathurst district.

1. Syngenetic Origin;
   - (a) Lenticular form with their large dimensions parallel to the stratification in the enclosing sediments.
   - (b) Occurring in marine shales or tuffs close to the contact of a volcanic unit.
   - (c) The sulfides are a facies of the sedimentary iron formation.
   - (d) The "porphyry" is a waterlain pyroclastic.

2. Source Bed Origin;
   - (a) Heavy iron sulfide content in the sedimentary rocks.
   - (b) A high grade of metamorphism in the country rocks which would indicate a sufficient rise in temperature of the rock environment to initiate remobilization.

[1] In part after Holyk (10).

(c) Structural traps to cause a "low pressure" area to which the mobilized metals could migrate.
(d) Replacement nature of the sulfides.

3. Magmatic Hydrothermal Origin;

(a) A genetic relation between the fissure type deposits to the north and the massive sulfide deposits.
(b) Replacement nature of the sulfides.
(c) Presence of appropriate structural traps.
(d) Presence of a suitable chemical environment to cause the precipitation of the sulfide material from the hydrothermal solutions, i.e.—the iron formation or chloritic schist.
(e) A spatial relationship with known granite occurrences.
(f) Structural intersections along which ore solutions could have travelled from depth.
(g) Possible feeders for the sulfide material as demonstrated at Brunswick No. 6 (15).
(h) Minimum depositional temperatures of the order of 600° C, assuming a confining pressure of 2,000 bars as indicated by the sphalerite geothermometer (5).
(i) The presence of sulfide bodies away from the main quartz porphyry and the interlayered zone as at New Larder "U" and Clearwater Brook (presented as negative evidence against the syngenetic and source bed origins).

The hydrothermal origin would appear to have the strongest arguments because all the standard elements usually demanded by the hydrothermalist are present. Yet the others have a more than average case. Items 3(a), 3(e) and 3(i) offer the most serious criticism against the syngenetic and source bed origin. To some, the source of the sulfur is a serious problem for the source bed hypothesis, but sufficient iron can be found in the ferruginous slates, iron formation and chloritic schists. In view of the conflicting field evidence it is possible that the actual processes involved were some combination of the above.

There would appear to be some relation between the sulfide deposits and the iron formation. Evidence suggesting that the sulfides are a facies of the iron formation is not too convincing. In order to account for the multi-million ton pyrite deposits, it is essential to have a large source of iron and sulfur. The common volatiles associated with igneous activity (or high temperature metamorphism) are H_2O, CO_2, H_2S, S, and Cl. These volatiles could have been channeled into favorable structural traps where the H_2S reacted with the Fe in the ferruginous slates or iron formation to produce pyrite.

$$4H_2S + Fe_2O_3 \rightleftarrows H_2 + 3H_2O + 2FeS_2$$

Such processes or somewhat related processes can account for many of the observed geologic relations associated with the sulfide deposits. For

instance, they account for the association of the deposits with the iron formation, the porphyry, and the structural traps. They also account for the conformable relations of the deposits and the host rock, the replacement nature of the sulfides, the fine grained textures, and the banding in the sulfides.

The all important argument of theory versus fact is still present. The origin of these deposits will not be known until extensive field and laboratory studies are complete.

THE APPLICATION OF SULFUR ISOTOPE STUDIES TO SULFIDE MINERAL DEPOSITS

Sulfur isotope abundance data indicates that meteorites and most basic igneous rocks have a fairly narrow range of S^{32}/S^{34} values (Fig. 4). From

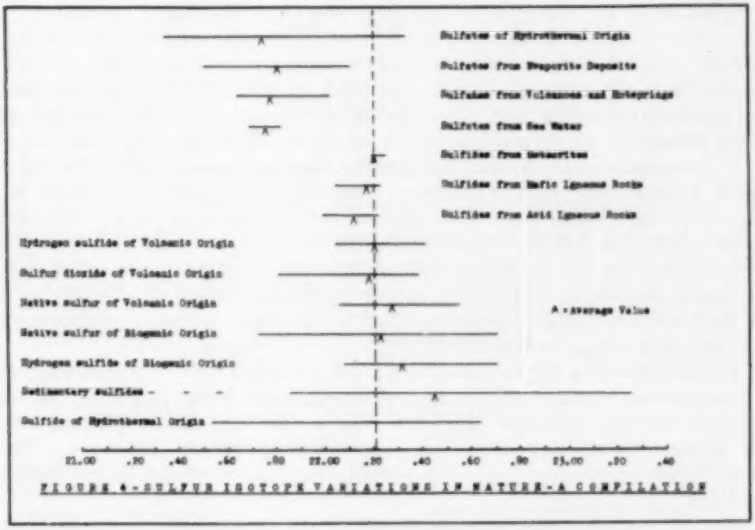
Sulfates of Hydrothermal Origin
Sulfates from Evaporite Deposits
Sulfates from Volcanoes and Hotsprings
Sulfates from Sea Water
Sulfides from Meteorites
Sulfides from Mafic Igneous Rocks
Sulfides from Acid Igneous Rocks
Hydrogen sulfide of Volcanic Origin
Sulfur dioxide of Volcanic Origin
Native sulfur of Volcanic Origin
Native sulfur of Biogenic Origin
Hydrogen sulfide of Biogenic Origin
Sedimentary sulfides - - -
Sulfide of Hydrothermal Origin
A = Average Value
21.00 .20 .40 .60 .80 22.00 .20 .40 .60 .80 23.00 .20 .40

FIGURE 4.-SULFUR ISOTOPE VARIATIONS IN NATURE-A COMPILATION

this observation, it is assumed that the terrestrial S^{32}/S^{34} ratio is equivalent to the meteoritic value and that the sulfur contained in the mantle of the earth has a uniform isotopic composition approximately equal to that of meteoritic sulfur (16).

It has been shown by both theory and experiment that (a) oxidation-reduction reactions, (b) bacterial reduction and (c) isotopic exchange reactions are all capable of producing a large fractionation of the sulfur isotopes in sulfur compounds (8, 9). The heavier less energetic isotope (S^{34}) concentrates in the oxidized form, while the lighter more energetic isotope concentrates in the reduced form. This relationship is further consolidated by the observation that sulfate in ocean water and evaporate deposits is en-

riched in S^{34}, and sulfur incorporated into predominately argillaceous sedimentary rocks, which consists largely of sulfides, is enriched in S^{32}.

The H_2S formed by the bacterial reduction of sulfate in the reducing environment of off-shore regions, reacts with iron or other metals to form sulfides. Thus *syngenetic sulfide deposits* should be enriched in S^{32}. It has also been shown (9) that the amount of fractionation is dependent on the rate of reduction, which is dependent on metabolite concentrations, temperature, concentration of sulfate, and conditions of growth. We would thus expect the resulting sulfur to be not only enriched in S^{32}, but to also exhibit a considerable range of S^{32}/S^{34} values. Since there are no definitely known syngenetic sulfide deposits that have been analyzed, the ratios expected can only be illustrated from the range of S^{32}/S^{34} values obtained from a few syngenetic sulfide samples (Fig. 4).

When sulfur is incorporated into hydrothermal solutions, the isotopic composition of the sulfur carried by these solutions will reflect the history of the segment of the crust or mantle from which the sulfur was derived. Sulfides derived directly from the mantle should have ratios approximately equivalent to the terrestrial value, provided, of course, that there has been no fractionation along the way. In other words, the stable isotopes of sulfur should act as natural tracers for studying sulfide-forming processes.

It is reasonable to assume that granite magmas formed within the crust digest a large volume of sedimentary material. If sulfate and sulfides become thoroughly mixed and homogenized during this process, the resulting sulfur could have a S^{32}/S^{34} ratio equivalent to the terrestrial value. On the other hand, if the S^{32}/S^{34} ratios of the hydrothermal sulfides were enriched in the heavy isotope, a sulfate-rich source would be indicated. Similarly, if the hydrothermal sulfides were enriched in the light isotope a sedimentary sulfide source would be indicated.

Sulfur deposits with a reasonably narrow range of S^{32}/S^{34} values suggest a homogenous source, with the homogenizing agent being a crustal magma and hydrothermal solutions (Fig. 5 [2]).- It is also true that deep-circulating hot waters could have the same homogenizing effect. However, "hot waters" are generally, or if not should be, considered as hydrothermal solutions.

Isotope variations in sulfide deposits of a few to several tenths of a percent or more suggest a much more complicated "plumbing system" (11) for the source and passage of the hydrothermal solutions. These solutions could have been derived from an inhomogeneous source or they may have been tapped from several localized and coalescing ore-fluid concentration zones.

On the basis of these hypotheses one would predict from Figure 5 that the sulfide deposits in Butte, Montana; Santa Rita, New Mexico; Gilman, Colorado; and Outokumpu, Finland, were derived from a homogeneous hydrothermal source, which originated either within the crust or upper mantle. This prediction is based on the narrow range of S^{32}/S^{34} values obtained and their approximate equivalence to the terrestrial value.

[2] Figure 5 is modified after M. L. Jensen, Econ. Geol., v. 54, p. 377, 1959.

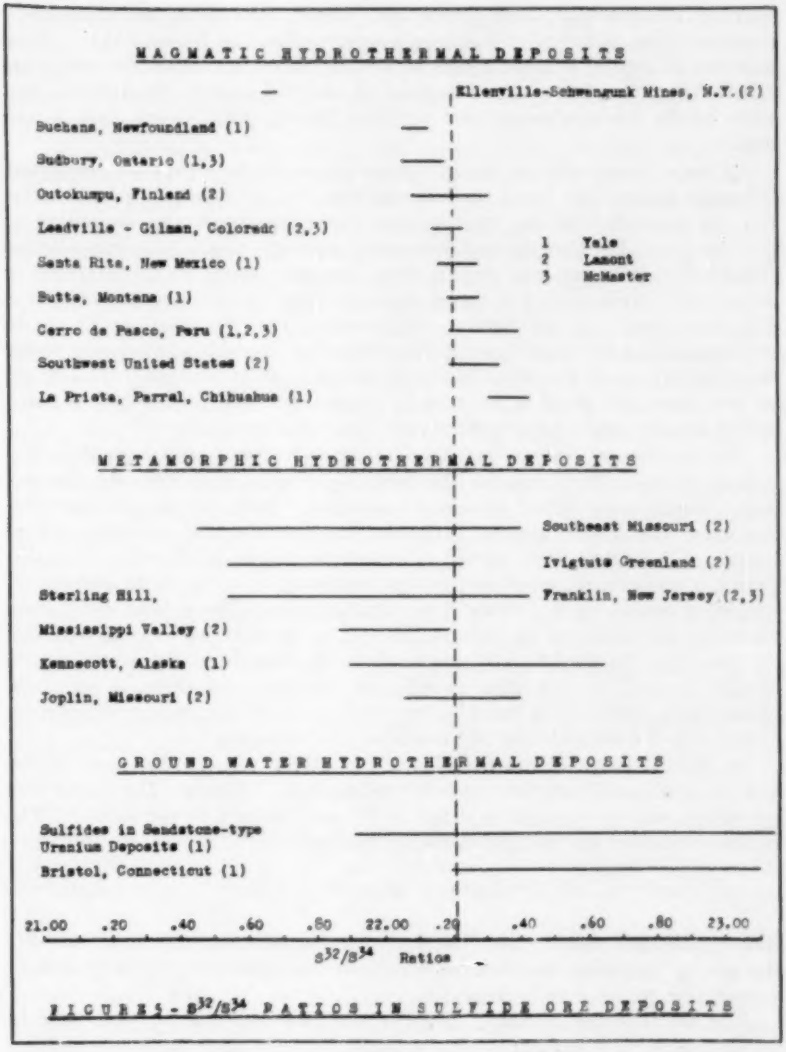

FIGURE 1 - S^{32}/S^{34} RATIOS IN SULFIDE ORE DEPOSITS

The ratios from La Prieta, Chihuahua, and the southwest United States would indicate a hydrothermal origin, but with a source slightly enriched in S^{32}. Those from Ellenville, New York, would indicate a similar origin, but with a sulfate rich source.

The deposits from the Mississippi Valley district, Southeast Missouri,

Sterling Hill-Franklin, New Jersey, and Ivigtut, Greenland, are an excellent example of the complicated plumbing system outlined by Jensen (11). These deposits all exhibit a broad range of S^{32}/S^{34} ratios, which on the whole are enriched in S^{34}. These ratios suggest an original source (or sources) that were highly inhomogeneous and certainly in the crust rather than in the mantle.

In some instances these broad conclusions might be somewhat premature, inasmuch as they are based on evidence that did not take into consideration (a) the possibility of any fractionation during transport and deposition or (b) the possibility that the sulfide-bearing solutions might have incorporated additional sulfide material during their transport from source to place of deposition. Kulp et al. (14) were aware of these possibilities, but may have dismissed them a bit too lightly. Kulp argued that the latter would not be important since the quantity of sulfide along the channels of transport would be extremely small compared to the quantities passing through. This might be very true, but could it not also be argued that the very origin of many sulfide deposits might be associated with "hot circulating waters?"

The problem of isotope fractionation during transport still remains. It is difficult to treat this problem theoretically or even quantitatively, because many uncertain conditions have to be assumed. Rafter et al. (21) have investigated the sulfur isotopic variations in New Zealand geothermal bore waters. These bore holes extend to a depth of 600 to 3,200 feet. They discharge a mixture of steam and water containing roughly thirty percent by weight of steam, or a 700 to 1 by volume ratio. These bore holes have discharge temperatures as high as 270° C. It is now well established that the steam in the discharge is produced by flashing from hot water tapped by the bore (21). In other words, far underground there is only one phase-liquid water. The total sulfur content of the discharges is approximately 1 to 2 millimoles per 100 moles of total discharge.

In the discharge of the bore holes, the sulfate follows the water phase, and the sulfide follows the vapor or steam phase. Rafter (21) found that the sulfide was 1.7 percent depleted in S^{34} with respect to the sulfate. The reaction followed the isotopic exchange reaction,

$$H_2S^{34} + S^{32}O_4^{2-} \rightleftarrows H_2S^{32} + S^{34}O_4^{2-}$$

Rafter (21) and Sakai (24) found similar fractionation effects in the discharges of fumaroles and volcanoes. However, these projects were not as quantitative as the bore hole studies.

The fractionation of sulfur isotopes was observed for the first time in the separation of a gas phase from a liquid phase in these bore hole studies. And equally important, is the fact that it occurred in a naturally occurring process. This discovery or confirmation has an immediate effect on the interpretation of sulfur isotope ratios. It now seems reasonable to assume that fractionation could be inherent in the separation of a gas phase from a liquid phase anywhere in the complex history of sulfide transportation and

deposition. If this is the case, the liquid phase, the gas phase, or a combination of both phases could be responsible for the formation of sulfide deposits. It is now no longer necessary to resort only to oxidation reduction processes associated with sedimentation to account for the variable S^{32}/S^{34} ratios observed in sulfide deposits.

Discussions to date have dealt with syngenetic and hydrothermal sulfide deposits. There remains a third mode of origin—the source bed origin. This concept implies that the metal ions are derived from a low concentration source bed (either sedimentary or volcanic) and are redeposited in a much more concentrated form in some suitable structural or stratigraphic trap. If the geological relations suggest such a mode of origin, the only avenue that can be followed with sulfur isotope studies is to sample both the source of the sulfides and the deposit. Theoretical considerations indicate that in both chemical reactions and diffusion processes the lighter isotope tends to be the more reactive. Consequently one would predict that the resulting sulfide deposit would exhibit S^{32}/S^{34} ratios that would either be equivalent to or lighter than the sulfides in the source bed. The deposit should also exhibit a considerable range of S^{32}/S^{34} values.

From this discussion it is apparent that predictions on sulfide genesis from sulfur isotope studies can only be made with a thorough understanding of the local geology and geochemistry of the deposit. Even when applied quantitatively, a sulfur isotope analysis can never indicate the unique history of any sample. However, it greatly restricts the choices available and combined with other geological and geochemical data can lead to a much better understanding of the genesis of sulfide ores.

Isotope Exchange Reactions.—The most useful exchange reactions are those associated with the contemporaneous formation of sulfide and sulfate (i.e. barite) minerals. The equilibrium constants at 0° C and 25° C for the exchange reaction

$$^{34}S^{2-} + {}^{32}SO_4^{2-} \rightleftarrows {}^{32}S^{2-} + {}^{34}SO_4^{2-}$$

are 1.085 and 1.074 respectively (30). *Provided that equilibrium has been established,* these isotopic exchange reactions can be utilized to determine the temperature of formation with a sensitivity of about ± two percent (24, 11).

The Significance of Associated Lead Isotope Studies.—Common lead, such as found in lead deposits, is a mixture of four stable isotopes having atomic weights 204, 206, 207, and 208. Of these, the last three are identical with the lead isotopes produced as stable end products of the radioactive decay of uranium and thorium; the first, lead 204 is not known to be produced on the surface of the earth (23). There are two general types of lead in minerals, ordinary lead and anomalous lead.

It would seem important to know whether or not there is a significant relation between the degree of normality of sulfur and lead isotope variations in the same mineral occurrence. If ordinary lead and sulfur both came

directly from the mantle, and were not fractionated or contaminated along the way, then there should be a relationship between ordinary leads and sulfur isotope ratios. On the other hand, if the ordinary lead and sulfur were remobilized or derived from fused sediments, one might expect the sulfur isotope composition to be different from the terrestrial value, and there are reasons to assume that the lead isotope composition may also be altered. The sulfur would be fractionated during its deposition and would

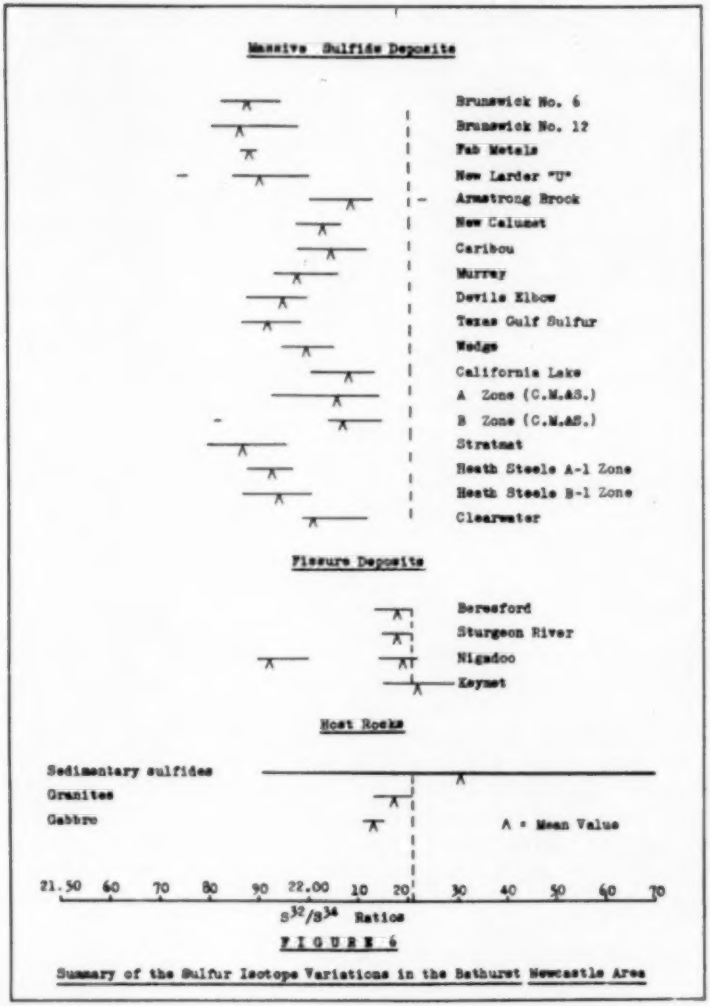

FIGURE 6

Summary of the Sulfur Isotope Variations in the Bathurst Newcastle Area

either be light or heavy depending on whether the sulfur came from a sulfide or sulfate source. The lead probably would not be altered if all the lead existed in the same form throughout the sedimentary strata. If the lead existed in different forms in the sedimentary horizons, resulting in different bond strengths for the lead isotopes, then the lead might be fractionated during the concentration processes (6).

However, the greatest changes in lead isotope ratios are due to the mixing or separation of lead isotopes that have had a prehistory of concentrated uranium association, and not due to isotopic fractionation effects. There-

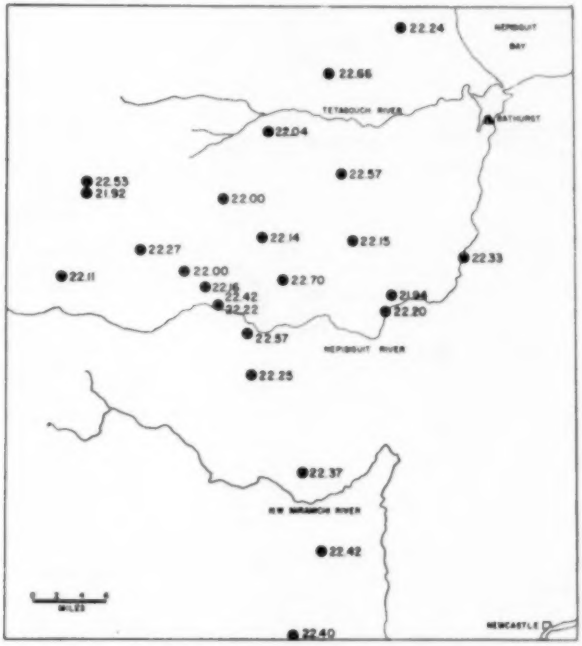

FIGURE 7.—SHOWING THE S^{32}/S^{34} RATIOS OF THE SEDIMENTARY SULFIDES

fore it would be expected that anomalous lead ores would show lead variations that are random with respect to sulfur ratios, except that the degree of variation might be correlated to some extent.

One possible correlation might arise as follows. Anomalous leads have been exposed to some high uranium-thorium or uranium-lead concentration. High uranium-lead concentrations are commonly associated with black shale environments. If these environments were the only high uranium-lead concentrations, then the sulfur associated with the anomalous leads would be enriched in S^{32}. However, it is necessary to consider the possibility that the lead might be derived from shales and the sulfur from some sulfate

source. In this case the leads would be anomalous but the sulfur would be enriched in S^{34}.

In some instances lead isotope variations will indicate the geochemical processes through which the lead has passed. However, the relationship between sulfur isotope variations and ordinary or anomalous leads is not very definite.

ANALYTICAL RESULTS

The analytical results are presented in the various tables and figures. The individual S^{32}/S^{34} ratios for each sample from the various sulfide de-

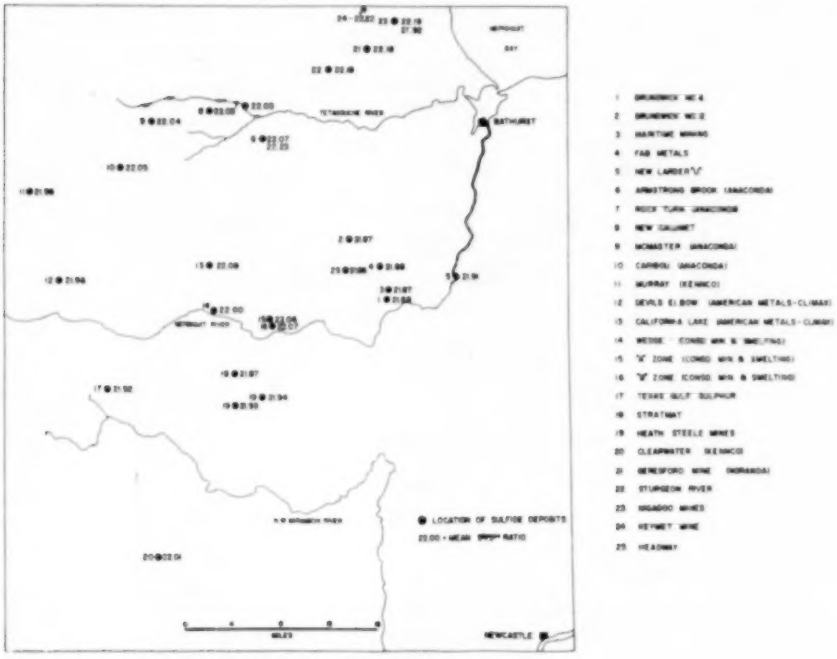

FIGURE 8 BATHURST - NEWCASTLE AREA
SHOWING THE MEAN S^{32}/S^{34} RATIOS FOR EACH SULFIDE DEPOSIT

posits and host rocks are contained in Tables 1 to 23.[3] A summary of all the sulfur isotope abundance data from the Bathurst area is presented in Table 24 and in Figures 6, 7, and 8. The potassium-argon data are presented in Table 25. The lead and sulfur isotope abundance data for the galena samples are contained in Table 26. A comparison of the S^{32}/S^{34} ratios between various sulfide minerals is presented in Table 27.

[3] Unless otherwise stated all the permil values are positive.

Table 1

No. 6 (Brunswick) Sulfide Body, Brunswick Mining & Smelting Corp.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	6	A	21.83,21.87(2),21.89,21.90 21.91	21.88	14.9
Pyrite	2	D_2	21.86, 21.89	21.88	14.9
Pyrite	1	A-B	21.85	21.85	16.2
Pyrite-Sphalerite	2	B	21.87, 21.89	21.88	14.9
Pyrite-Pyrrhotite	1	E	21.89	21.89	14.4
Pyrrhotite	2	E	21.87, 21.95	21.91	13.5
"	1	F	21.86	21.86	15.8
Galena	2	B	21.84, 21.95	21.89	14.4
Sphalerite	1	B	21.85	21.85	16.2
Chalcopyrite	1	F_2	21.87	21.87	15.3

Table 2

No.12 (Anaconda-Lenaridge) Sulfide Body, Brunswick Mining & Smelting Corp.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	4	A	21.84, 21.85, 21.86, 21.87	21.88	14.9
"	1	B	21.82	21.82	17.6
"	1	D_2	21.82	21.82	17.6
"	1	A-D	21.89	21.89	14.4
Galena	1	B	21.84	21.84	16.7
"	1	C	21.90	21.90	14.0
Sphalerite	1	A	21.89	21.89	14.4
"	3	B	21.88(3)	21.88	14.9
"	1	C	21.86	21.86	15.8
Massive Sulfides	4	C	21.81, 21.83, 21.88, 21.91	21.86	15.8

Table 3

New Larder "U" Island Mines, Ltd., Sulfide Body

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	2	A	21.98, 22.01	21.99	9.9
"	1	B	21.93	21.93	12.6
Pyrrhotite	1	F	21.87	21.87	15.3
Pyrite-galena	1	B-C	21.86	21.86	15.3
Galena	1	B	21.92	21.92	13.1
Sphalerite	2	B	21.89(2)	21.89	14.4
Chalcopyrite	1	E	21.75	21.75	20.7
"	2	C	21.92, 21.98	21.95	11.7
Massive Sulfides	1	C	21.88	21.88	14.9

Data on individual ratios, specimen numbers, and locations may be obtained from the author if desired.

Table 4

Armstrong Brook sulfide body, Anaconda Co., (Canada) Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	4	A	22.01,22.10(2),22.13	22.09	5.4
"	1	A-B	22.23	22.23	-0.9
Galena Pyrite	1	B	22.02	22.02	8.6
Chalcopyrite	1	B	22.05	22.05	7.2

Table 5

Oryan Brook Sulfide Body, New Calumet Mines, Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	2	D_1	22.07, 22.02	22.04	7.7
Massive Sulfides	1	C	22.06	22.06	6.8
Massive Sulfides	1	B	21.98	21.98	10.4

Table 6

Caribou Sulfide Body, Anaconda Co. (Canada)Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	10	A	22.05, 22.06(3),22.07(3) 22.08, 22.12(2)	22.08	5.9
"	3	B	22.01, 22.03(2)	22.02	8.6
"	1	A-B	22.00	22.00	9.5
"	1	E	22.03	22.03	8.1
"	1	A-C	22.06	22.06	6.8
Pyrite-Galena	1	B	22.00	22.00	9.5
" "	1	C	21.98	21.98	10.4
" Sphalerite	1	B	22.00	22.00	9.5
Sphalerite	1	B	22.05	22.05	7.2
Chalcopyrite	3	B	22.07, 22.08, 22.09	22.08	5.9
Massive Sulfides	3	B	22.02, 22.09, 22.11	22.07	6.3
" "	2	C	21.98, 22.10	22.04	7.7

Table 7

Murray Sulfide Body, Kennco Explorations (Canada) Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	5	A	21.93, 21.96(2), 21.99	21.97	10.8
"	1	A_2	22.00 22.01	22.01	9.0
"	1	B	22.06	22.06	6.8
"	1	D_2	21.94	21.94	12.2
Sphalerite	1	B	21.97	21.97	10.8

Table 8

Elbow Sulfide Body, American Metal Climax, Inc.,

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	1	A	22.00	22.00	9.5
"	3	A_2	21.89, 21.94, 21.99	21.94	12.2
"	2	B	21.88, 21.96	21.92	13.1
"	1	A_1-D_2	22.00	22.00	9.5
Pyrrhotite	3	B	21.88, 21.94, 21.98	21.93	12.6
"	1	B-F_1	21.99	21.99	9.9
Chalcopyrite	1	B	22.01	22.01	9.0
"	1	F_2-C	21.97	21.97	10.8

Table 9

California Lake Sulfide Body, American Metal Climax,Inc.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	5	A_1	22.01, 22.06, 22.10 22.11, 22.13	22.08	5.9

Table 10

Wedge Sulfide Body, Consolidated Mining & Smelting Co.of Canada,Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	1	A	22.00	22.00	9.5
"	1	B	21.97	21.97	10.8
Sphalerite-Pyrite	1	B	21.99	21.99	9.9
Sphalerite	1	B	21.95	21.95	11.7
Chalcopyrite	1	D	22.05	22.05	7.2
Massive Sulfides	2	B	22.01, 22.06	22.04	7.7

Table 11

Nepisiquit "A" Sulfide Body, Consolidated Mining & Smelting Co., of Canada, Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} °/oo Average
Pyrite	4	A	22.02, 22.04, 22.11 22.15	22.05	7.2
"	1	D_2	22.10	22.10	5.0
"	1	B	22.12	22.12	4.1
Pyrite-Sphalerite	2	B	21.97, 22.03	22.00	9.5
Pyrrhotite	2	F	22.08, 22.12	22.10	5.0

Table 12

Heriaiquit "B" Sulfide Body, Consolidated Mining & Smelting Co., Of Canada, Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	6	A	21.82, 22.04, 22.08 22.11, 22.12, 22.15	22.05	7.2
"	1	A-B	22.11	22.11	4.5
"	1	D_1	22.10	22.10	5.0
Pyrrhotite	1	F_1	22.10	22.10	5.0

Table 11

Texas Gulf Sulfur Company Sulfide Body, near the Head of the N.W. Mamichi River

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	2	A	21.91, 21.92	21.91	13.5
"	1	B	21.98	21.98	10.4
"	1	D_1	21.87	21.87	5.3
"	1	D_2	21.92	21.92	13.1
Pyrrhotite	1	F	21.93	21.93	12.6
Galena	1	B	21.92	21.92	13.1
Chalcopyrite	2	G	21.90, 21.91	21.91	13.5

Table 14

Block 61 Sulfide Body of Strmtmat Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	7	A	21.80, 21.86(?), 21.88 21.90, 21.92, 21.92	21.88	14.9
"	3	B	21.85, 21.89, 21.93	21.89	14.4
Sphalerite	2	B	21.87, 21.92	21.89	14.4
Chalcopyrite	1	G	21.81	21.81	16.0

Table 15

"A-1" Zone, Heath Steele Mines, Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	3	A	21.88, 21.91, 21.92	21.90	14.0
"	1	B	21.95	21.95	11.7
Sphalerite	3	B	21.94, 21.95, 21.97	21.95	11.7

Table 16

Clearwater Stream Deposit

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	3	A	21.99 (2), 22.00	21.99	3.9
"	1	A_2	21.98	21.98	10.4
"	1	B	21.99	21.99	3.9
"	1	D_2	22.12	22.12	4.1
Chalcopyrite	3	G	22.01(2), 22.02	22.01	3.0

Table 17

Lavigne Brook Sulfide Body, Pemsquid Mines, Ltd.[4]

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	1		22.21	22.21	0
Chalcopyrite	9		22.11, 22.15, 22.16, 22.18(2), 22.19(2) 22.21, 22.22	22.18	1.4

[4] Pismire deposits not described by type

Table 18

Sturgeon River Sulfide Body, Sturgeon River Mines Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	3		22.15, 22.16, 22.21	22.17	1.8
Pyrrhotite	2		22.16, 22.18	22.17	1.8
Galena	4		22.16, 22.18, 22.19, 22.21	22.18	1.4
Sphalerite	2		22.20, 22.21	22.20	0.6

Table 19

Nisnsdon Sulfide Body, Nisnsdon Mines Ltd.

Mineral	No.	Type	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	3		21.90, 22.00, 22.22	22.04	7.7
Pyrrhotite	4		21.91, 22.20, 22.21, 22.22	22.13	3.6
Galena	2		21.90, 22.14	22.02	8.6
Sphalerite	4		22.15, 22.19, 22.20, 22.21	22.19	1.0
Chalcopyrite	1		22.17	22.17	1.8
Arsenopyrite	1		22.16	22.16	2.3

Table 20

Kaymet Sulfide Body, Kaymet Mines Ltd.

Mineral	No.	S^{32}/S^{34} Ratios	S^{32}/S^{34} Average	δS^{34} o/oo Average
Pyrite	3	22.15, 22.19, 22.21	22.18	1.4
Galena	8	22.17, 22.19, 22.20, 22.24, 22.25, 22.26, 22.28, 22.29	22.23	-1.0
Sphalerite	2	22.22, 22.26	22.24	-1.4

Table 21

Sulfur Isotope Abundance Data for Deposits from which only a Few Samples were Obtained

Name	Location Lat. & Long.	Sulfide Mineral	Type	S^{32}/S^{34}	δS^{34} o/oo
Maritime Min. Corp.	Lat. 47°25' Long. 65°49'	Pyrrhotite	G	21.86	+15.8
Fab. Metals, Inc.	Lat. 47°27'E Long. 65°50'W	Pyrrhotite	G	21.87	+15.3
Fab. Metals, Inc.	Lat. 47°27'E Long.65°50'W	Pyrrhotite	G	21.90	+14.0
Headway Red Lake	Lat. 47°27' Long. 65°53'	Massive Sulfides	C	21.86	+15.8
Anaconda Co. (Can.), Ltd. McMaster Pyrite Body	Lat. 47°37'W Long. 66°14'	Pyrite	D_1	22.04	+ 7.7
Anaconda Co. (Can.) Ltd. Rocky Turne Sulfide Deposit	Lat. 47°38'W Long. 66°04'	Pyrite	A	22.03	+ 8.1
Noranda Mines Ltd., Arsenide Showing	Lat. 47°42' Long. 65°51'W	Arseno-pyrite		22.29	- 3.6

Table 22

Syngenetic Sulfides in Sedimentary Rocks of the Bathurst-Newcastle Area

Pyrite Samples	S^{32}/S^{34} Ratios	δS^{34} °/oo
2	21.91, 21.94	13.1, 12.2
3	22.00(2), 22.04,	9.5(2), 7.7
4	22.11, 22.14, 22.15, 22.16	4.5, 3.2, 2.7, 2.3
5	22.20, 22.22, 22.24, 22.25, 22.27	0.6, -0.5, -1.4, -1.8, -2.7
5	22.33, 22.37, 22.40, 22.42(2)	-5.4, -7.2, -8.6, -9.5(2)
3	22.53, 22.57(2)	-14.5, -16.2(2)
2	22.66, 22.70	-20.2, -22.2

Table 23

Sulfides Concentrated from Intrusive Igneous Rocks of the Bathurst-Newcastle Area

No.	Sulfide Mineral	Location			S^{32}/S^{34}, δS^{34} o/oo	
51	Pyrite	Lat.47°34'N	Long.65°40'W	Granite	22.21	0.0
52	Pyrite	Lat.47°42'N	Long.65°51'W	Granite	22.13	3.6
41	Pyrite	Lat.47°29'N	Long.66°02'W	Gabbro	22.11	4.5
43	Pyrite	Lat.47°19'N	Long.66°05'W	Gabbro	22.15	2.7

Table 24

Summary - Sulfur Isotope Abundance Data from the Bathurst-Newcastle Area

No.	Name	No. samples analysed	Mean S^{32}/S^{34} Ratio	Standard Deviation	Range of S^{32}/S^{34} Values	Range in Per Mil values
	Massive Sulfide Deposits					
1	Brunswick No. 6	19	21.88	0.070	21.83 - 21.95	5.3
2	Brunswick No. 12	18	21.87	0.055	21.81 - 21.98	7.6
3	Maritime Mining	1	21.87			
4	Fab Metals	2	21.88		21.87 - 21.90	1.3
5	New Larder "U"	12	21.91	0.075	21.75 - 22.01	11.2
6	Armstrong Brook (Anaconda)	7	22.09	0.068	22.01 - 22.23	8.1
7	Rocky Turn (Anaconda)	1	22.03			
8	New Calumet	4	22.03	0.042	21.98 - 22.07	4.1
9	McMaster (Anaconda)	1	22.04			
10	Caribou (Anaconda)	28	22.05	0.040	21.98 - 22.12	6.3
11	Murray (Kennco)	10	21.98	0.040	21.93 - 22.06	5.8
12	Devils Elbow (Amer. Metals-Climax)	13	21.96	0.047	21.88 - 22.00	5.4
13	California Lake (Amer.Metals-Climax)	5	22.08	0.048	22.01 - 22.13	5.4
14	Wedge (Consd.Mining & Smelt.)	7	22.00	0.040	21.95 - 22.06	4.9
15	"A" Zone (Consd. Mining & Smelt.)	10	22.06	0.075	21.93 - 22.14	8.5
16	"B" Zone (Consd. Mining & Smelt.)	9	22.07	0.098	21.82 - 22.15	14.9
17	Texas Gulf Sulfur	9	21.92	0.029	21.87 - 21.98	4.9
18	Stratmat	13	21.87	0.042	21.80 - 21.96	7.2
19	Heath Steele Mines A-1 Zone B-1 Zone	7 29	21.93 21.94	0.031 0.029	21.88 - 21.97 21.87 - 22.01	4.1 6.3
20	Clearwater (Kennco)	10	22.01	0.043	21.99 - 22.12	5.8
25	Headway	1	21.86			
	Fissure Deposits					
21	Beresford Mine (Noranda)	10	22.18	0.026	22.13 - 22.21	3.6
22	Sturgeon River	11	22.18	0.023	22.15 - 22.21	2.7
23	Nigadoo Mines Type A Type B	11 4	22.19 21.92	0.031 0.043	22.14 - 22.22 21.90 - 22.00	3.7 4.5
24	Keymet Mine	13	22.22	0.025	22.15 - 22.29	6.3
	Host Rocks					
26	Sedimentary Sulfides	23	22.31	0.131	21.91 - 22.70	
27	Sulfides in Granite	2	22.17		22.13 - 22.21	3.6
28	Sulfides in Gabbro	2	22.13		22.11 - 22.15	1.8

Samples from B-1 Zone at Heath Steele (Dechow 1959)

Table 25

Age of the Intrusive Granites

Sample Number	Location	Lat. Long.	K%	A/K	Air Correction %	Age-m.y.	
B3076	Connelly Quarry	47°34'N 65°40'W	7.02	0.0260	Unsatisfactory	398 ± 12	1
B3806	Popple Depot	47°24'N 66°30'W	7.04	0.0258	9.1	395 ± 15	
B3807	Nicholas Dungs	47°42'N 65°51'W	4.86	0.0255	0.5	395 ± 12	
B3833	Bald Mountain	47°13'N 66°29'W	4.73	0.0234	8.6	364 ± 15	

1 398 M.Y. is a maxium value only

Table 26

Lead and Sulfur Isotope Abundance Data for Galena Samples *

No.	Location	Pb206/207	Pb208/204	Pb206/204	S^{32}/S^{34}
532	Keymet Mine	1.1576	38.2624	18.262	22.20
810	Keymet Mine	1.1610	38.4315	18.399	22.24
807	Brunswick No. 6	1.1588	38.0437	18.211	21.84
808	Brunswick No. 12	1.1596	38.5387	18.383	21.90
809	New Larder "U"	1.1584	38.4094	18.357	21.86

Pb206/Pb207, Pb208/Pb204 } Mean Age = 370 ± 20 x 10^6 yrs.

* Lead Isotope Abundance Data and Ages supplied by the Department of Physics, University of Toronto.

Table 27

Comparison of S^{32}/S^{34} Ratios Between Various Sulfide Minerals

No.	Massive Sulfide Deposits	Pyrite No.	Pyrite Mean S^{32}/S^{34} Ratio	Sphalerite-Galena No.	Sphalerite-Galena Mean S^{32}/S^{34} Ratio	Chalcopyrite-Pyrrhotite No.	Chalcopyrite-Pyrrhotite Mean S^{32}/S^{34} Ratio
1	Brunswick No. 6	6	21.87	3	21.98	4	21.89
2	Brunswick No. 12	6	21.85	7	21.89		
5	New Larder "U"	3	21.97	4	21.89	4	21.90
6	Armstrong Brook	5	22.11	1	22.02	1	22.05
8	New Calumet	2	22.04				
10	Caribou	15	22.11			3	22.05
11	Murray	8	21.98	1	21.98		
12	Devils Elbow	7	21.95			6	21.96
13	California Lake	5	22.08				
14	Wedge	3	22.01	2	21.98	1	22.05
15	"A" Zone	6	22.07	1	22.03	2	22.10
16	"B" Zone	8	22.06			1	22.05
17	Texas Gulf Sulfur	5	21.92	1	21.92	3	21.91
18	Stratmat	9	21.88	2	21.89	1	21.81
19	Heath Steele - A Zone	4	21.91	3	21.95		
20	Clearwater	6	22.01			3	22.01
Total	Each deposit a weight of 1	16	21.98	10	21.94	11	21.98
	Each sample a weight of 1	98	21.93	28	21.89	26	21.94
	Fissure Deposits						
	Keymet	3	22.18	10	22.24		
	Sturgeon River	3	22.17	6	22.19	2	22.17
	Rigadoo - Type A	3	22.21	4	22.17	3	22.20
	Restigouche Mine					10	22.18
Total	Each deposit a weight of 1	3	22.19	3	22.20	3	22.18
	Each sample a weight of 1	9	22.19	20	22.21	15	22.18

The mineralogical and textural associations of the massive sulfide deposits are fairly homogeneous, both within one deposit and from one deposit to the next. For the purpose of brevity the individual samples are described by cataloging them into different types. The standard types of association are outlined as follows:

Type A_1—Massive fine- to medium-grained pyrite containing less than five percent other sulfides.

Type A_2—Medium- to coarse-grained massive pyrite containing less than five percent other sulfides.

Type B—Massive fine- to medium-grained pyrite containing diffuse bands or stringers of sphalerite and galena, in places with minor chalcopyrite and pyrrhotite. The sample contains more than five percent sphalerite and galena. Gangue minerals are commonly quartz and carbonate.

Type C—Fine- to medium-grained, intimately associated pyrite, sphalerite, and galena.

Type D_1—Pyrite disseminated through host rock in which pyrite content varies up to eighty percent.

Type D_2—Pyrite stringers cutting the host rock.

Type E—Massive fine-grained pyrite containing either narrow to broad diffuse bands, stringers or blebs of pyrrhotite and/or chalcopyrite.

Type F_1—Massive fine- to medium-grained pyrrhotite containing blebs or stringers of chalcopyrite.

Type F_2—Chalcopyrite containing blebs or stringers of massive fine to medium grained pyrrhotite.

Type G—Irregular stringers or disseminations of chalcopyrite and pyrrhotite replacing the host rock.

DISCUSSION OF RESULTS

Sulfur Isotope Variations in the Syngenetic Sulfides and Intrusive Igneous Rocks.—The wide range of S^{32}/S^{34} values (21.90–22.70) in the syngenetic sulfides is indicative of their mode of origin (Table 22, Fig. 6). Harrison and Thode (8) found the amount of fractionation inherent in the reduction of sulfate to hydrogen sulfide to be dependent on the rate of reaction. The rate of reaction in turn was found to be dependent on metabolite concentrations, temperature, food source, and sulfate concentration. There should exist in any sedimentary basin a wide distribution of these conditions. Consequently a fairly broad range of S^{32}/S^{34} values should be found in the sulfide material formed.

It is true that the syngenetic sulfides analyzed in the Bathurst area were not taken from one specific horizon, but in general they were taken from the "transition zone," a sedimentary volcanic sequence probably formed over a fairly short period of time (Fig. 7).

In addition to having a wide range of S^{32}/S^{34} values, the syngenetic sulfides are, when compared with meteoritic sulfur, generally enriched in S^{32}. This is in good agreement with previous studies on syngenetic sulfides (Fig.

4). The syngenetic origin of these sulfides is assumed on the basis that they are disseminated through shales and argillites, with no evidence of hydrothermal activity.

Sulfur isotope ratios for the two granites are 22.13 and 22.21, and for the two gabbros 22.11 and 22.15 (Table 23). These values are not unusual for ratios found in granites and gabbros (Fig. 4).

The Age of the Granites and the Lead Minerals in the Sulfide Deposits.—Three of the granites that are intrusive into the host rocks of the ore deposits have an age very close to 390 million years, based on K/A dating (Table 25). The Bald Mountain granite gave a slightly lower age, but this may be a result of alteration in the biotite for the granite bodies in the immediate locality are all quite highly altered. The Nicholas Denys granite is intrusive into fossiliferous Middle Silurian sedimentary rocks (33). The granite stock from which sample B3076 is taken is overlain by the Pennsylvanian (26). The granites are thus post middle Silurian and pre-Pennsylvanian in age.

Model lead ages computed in the Department of Physics at the University of Toronto for five galenas from the sulfide deposits give a mean age of 370 ± 20 m.y. (Table 26). The lead ages are based on a recently developed model, which assumes that the lead came from the mantle (22). The uncertainty attached to the mean age of 370 ± 20 m.y. is based on the new model, rather than the age itself (7). The model for the ages used is still fundamentally the same as that proposed by Alpher and Herman (3).

There is no evidence that the model lead ages and the granite ages disagree within stated errors. It is concluded that the sulfides and granite bodies were emplaced during the same major orogenic event.

Sulfur and Lead Isotope Abundance Data from the Same Samples.—Sulfur isotope ratios were determined (Table 26) for the sulfide material in the galena samples discussed above. Two of these galena samples are from the fissure deposits (Keymet mine) and the other three from the massive sulfide deposits. The lead isotope abundance data appear to be relatively homogeneous for all five samples. There is, however, a distinct difference in the sulfur isotope ratios. The S^{32}/S^{34} ratios from the fissure deposits are enriched in the lighter isotope relative to those from the massive sulfide deposits. The range of values within each group is small. In this instance the relationship between the sulfur and the lead isotope ratios is not clear.

Sulfur Isotope Variations Between Different Mineral Species.—An attempt is made in Table 27 to determine whether or not there are definite S^{32}/S^{34} variations between different sulfide species within the same deposit. Only sulfide samples known to be reasonably pure were used in this compilation. The sulfide specimens were divided into three groups: (1) pyrite, (2) sphalerite and galena, and (3) pyrrhotite and chalcopyrite.

If, in the massive sulfide deposits, the mean of each group is given a weight of one, the sphalerite-galena group (21.94) tends to be approximately one mil heavier than the pyrite (21.98), while the chalcopyrite-pyrrhotite group (21.98) is essentially the same as the pyrite group. The trend is amplified (Table 27) if we give each sample a weight of one. How-

ever, this latter approach is not very meaningful since the pyrite samples are heavily weighted from deposits with a high S^{32}/S^{34} ratio. For instance, fifteen samples were used from the Caribou deposit which has a S^{32}/S^{34} ratio for the pyrite group of 22.11. Although the galena-sphalerite group appears to be slightly enriched in S^{34}, the trend is so small that it is almost negligible. This variation is not apparent in the fissure deposits (Table 27) where the three groups have nearly identical mean ratios.

A similar compilation was made to determine if there were any S^{32}/S^{34} variations with depth in the deposit, but no trends were detected.

Statistical Analysis of the Sulfur Isotope Variations.—Early in this project Brunswick No. 6, Brunswick No. 12, and the Caribou deposit were studied in detail (Tables 1, 2, 6). Apart from slight variations between mineral species, no spatial relations were noted. A statistical analysis of the data from these deposits indicated that the mean S^{32}/S^{34} ratio, as well as the standard deviation of the mean, could be approximately determined by selecting at random nine to twelve spatially distributed samples from the deposit. The above statistical analysis suggests that sufficient information would be obtained by analyzing only ten to twelve samples per deposit. This procedure was followed in the remainder of the project.

The sulfur isotope ratios for the sulfide deposits are presented in Tables 1 to 21 and summarized in Table 24 and Figure 6. Each deposit has a very narrow range of values, the minimum range of 2.7 mils at Sturgeon River and the maximum range of 15 mils at the Consolidated Mining and Smelting "B" Zone.

The massive sulfide deposits have mean S^{32}/S^{34} values ranging from 21.87 to 22.09. The fissure deposits, however, are definitely higher having mean S^{32}/S^{34} values ranging from 22.18 to 22.21 (Figs. 6, 8).

The Origin of the Deposits.—In the discussion on the geology of the deposits it was noted that the Clearwater deposit, and possibly the New Larder "U" and the Stratmat deposits were found outside the main transition zone. The present study (Table 24) indicates that the sulfides from these deposits have an isotopic composition similar to the other massive sulfide deposits, suggesting a common origin of the sulfur for all of these deposits.

In addition to the massive sulfide deposit at Clearwater, there are also four roughly parallel superimposed zones of disseminated pyrrhotite and chalcopyrite. The sulfur isotope ratios in the disseminated zones were identical to the sulfur isotope ratios in the massive sulfide body (Table 16), indicating that all the sulfur had a common source.

Three modes of origin have been advocated on geological grounds for the massive sulfide deposits: (a) syngenetic origin, (b) magmatic hydrothermal origin, and (c) a source bed origin.

In a syngenetic origin the sulfur could either have been derived from seawater sulfate by bacterial reduction, with strong fractionation and the expected enrichment in S^{32}, or else it could have been supplied by submarine volcanic springs of magmatic origin, and precipitated immediately, with an expectable lack of fractionation. Known syngenetic sulfides in the area

are generally enriched in the lighter isotope and display a broad range of S^{32}/S^{34} values. The massive sulfide deposits are enriched in the heavier isotope and the individual deposits all have a relatively narrow range of S^{32}/S^{34} values. This is immediately suggestive, but certainly not diagnostic, that the massive sulfides are not of syngenetic origin.

If the sulfide deposits were concentrated from some source bed, the nature of the source bed should be reflected in the isotopic composition of the redeposited sulfur. Two sources for the sulfide material are considered in the Bathurst area: (a) the tuffs and associated volcanic material, and (b) the sedimentary host rocks. It was originally intended to investigate the isotopic composition of the sulfides in the tuffs, but samples of this material were difficult to find, and when found, generally contained small fractures filled with pyrite, thereby placing doubt on the primary origin of the sulfide material. In any case, it is anticipated that redeposited sulfides should display a considerable range of S^{32}/S^{34} values (11). Such evidence is not found in the Bathurst deposits.

The isotopic composition of the sulfur in the sedimentary host rocks has been investigated. These sulfides are enriched in the lighter isotope and display a broad range of values. If the massive sulfide deposits were derived from such a source, theoretical considerations (30) indicate that the resulting ratios should be equivalent to or lighter than the sedimentary values. Coming from an inhomogeneous source a fairly broad range of values should also be expected. However, the massive sulfide deposits are definitely enriched in the heavier isotope with respect to the syngenetic sulfides and all have a fairly narrow range of S^{32}/S^{34} values. This indicates that the sulfides have not been reconcentrated from the syngenetic sulfides. For completeness, an open system should be briefly considered for the above process. There is a possibility that a portion of the light sulfur derived from the sediments, passed out of the system, leaving the deposits enriched in the heavier isotope. If each deposit is considered as a separate system, it appears fortuitous that such a process (a) would be carried out to the same extent in more than twenty deposits, and (b) that it would result in an almost homogeneous end product in every case.

The narrow range of S^{32}/S^{34} values found in the deposits suggests that the deposits were derived from some homogeneous source. Jensen (11) has suggested that magmatic hydrothermal deposits have a very narrow range of S^{32}/S^{34} values within each deposit. This is precisely what is found in the deposits of the Bathurst area. Also taking into consideration the fact that the granites were intruded into the host rock at approximately the same time as the formation of the lead minerals, and the negative evidence presented against the syngenetic and source bed origin, it seems reasonable that well homogenized magmatic hydrothermal solutions are the most logical source for the sulfide deposits.

The relationship between the massive sulfide deposits and the fissure deposits is another problem. The lead isotope data, being reasonably homogeneous, indicates that the lead from both types of deposits probably came from some homogeneous source (31). This lead data gives strong inde-

pendent evidence that the ores came directly from below the crust, and therefore are of magmatic hydrothermal origin. It is very doubtful that an element with as high a mass number as lead would undergo detectable stable isotope fractionation during all physical or chemical processes subsequent to its separation from a uranium or thorium rich source. However, it has been suggested (6) that in certain geological processes lead isotopes may be fractionated.

The sulfur isotope ratios fall into two distinct groups. One group represents the massive sulfide deposits, the other group represents the fissure deposits. This suggests that the sulfur came from two separate sources. The Nigadoo deposit, however, possesses two distinct sets of sulfur isotope ratios, one equivalent to the fissure deposits, and the other equivalent to the massive sulfide deposits (Table 19). Similarly the Armstrong Brook deposit has one sample with a sulfur isotope ratio of 22.23 (Table 4), which is equivalent to the fissure deposit values. Thus, in the formation of these deposits there was either an intermixing of sulfur from two sources or there was one homogeneous source, and the sulfur was systematically fractionated during transport. This problem is difficult to evaluate. It seems more reasonable to have two separate, though closely related sources in time and space, than one source which requires a systematic fractionation in more than twenty deposits. If this is the case, there must have been some intermixing of sulfur from the two sources in the formation of the Nigadoo and Armstrong Brook deposits. If this is true, the close relation in time for the origin of the deposits is confirmed.

It is difficult to explain why the massive sulfide deposits are enriched in S^{34} relative to the meteoritic S^{32}/S^{34} value. The source could have been contaminated by assimilation of heavy sulfur, by the loss of the isotopically lighter volatiles, or fractionation may have been inherent in the process or processes of transportation from the source to the site of deposition. These problems are open for further investigation.

Early in the program a systematic radial distribution of the mean S^{32}/S^{34} ratios throughout the massive sulfide deposits was evident. As more deposits were studied this trend diminished and perhaps disappeared. Possibly the mean S^{32}/S^{34} ratios for each deposit decreases outward from the California Lake—Consolidated Mining and Smelting "A" and "B" Zone area (Fig. 8). For instance, the latter deposits have mean S^{32}/S^{34} values of approximately 22.07, but the mean for the Brunswick deposits is 21.88, for Heath Steele 21.96, for Texas Gulf 21.92, for Devils Elbow 21.96, for the Murray deposit 21.98, and for the Caribou-New Calumet area 22.04.

Whether this trend exists or not, the deposits in each of the above areas have a very close range of mean values. Rather than have a point source with a slight systematic fractionation along the channelways of transport, it appears more reasonable to assume several local sources, closely related in space, but each having individual characteristics slightly different from each other. In the Bathurst area these local sources possibly are small stocks or cupolas associated with the main granite batholith. The geology supports such a model (Fig. 3). The New Larder "U" and Murray deposits are

approximately thirty-five miles apart. Interpretation of the geology suggests that granite would be encountered at depths of one to five miles over most of the Bathurst area.

The laboratory data is presented and discussed. It is the privilege of those versatile investigators who are both initiated in isotope geology and who are familiar with the geology of the Bathurst area to agree or disagree with the conclusions reached.

SUMMARY AND CONCLUSIONS

1. There are two types of sulfide deposits in the Bathurst-Newcastle area: (a) fissure deposits and (b) massive sulfide deposits.

2. The massive sulfide deposits are by far the larger of the two groups, and have the greatest economic potential. In general, the massive sulfides replace sedimentary rocks in a sedimentary-volcanic sequence known locally as the "transition zone." They are commonly associated with drag-folds or shears. Exceptions to this generality do occur. Geological evidence has been interpreted variously to indicate a syngenetic, a magmatic hydrothermal, and a source bed origin for these deposits.

3. Sulfides (syngenetic) disseminated through the black shales and argillites of the host rock are enriched in S^{32} with respect to the meteoritic value. They have a broad range of S^{32}/S^{34} values. This data corroborates the laboratory conclusions of Harrison and Thode (8). These sulfides must have been reduced by the bacterial reduction of sulfate to sulfide.

4. S^{32}/S^{34} ratios for the sulfide deposits fall into two distinct groups. In general, one group (21.88–22.05) represents the massive sulfide deposits, the other group (22.18–22.21) represents the fissure deposits. This suggests two separate, but probably closely related sources for the sulfur (and the deposits).

5. The granites intrusive into the host rocks of the sulfide deposits have a mean age of 386 m.y. Lead minerals in the sulfide deposits have a mean model lead age of 370 ± 20 m.y. This indicates that the lead minerals were formed, and the granites were intruded during the same period of orogenesis.

6. The sulfur in syngenetic sulfide deposits which has been derived from sulfate should be enriched in S^{32} over the sulfate source, and have a broad range of S^{32}/S^{34} values. The S^{32}/S^{34} ratios in the sulfide deposits of the Bathurst area do not follow this trend. Therefore, based on isotopic data, the sulfide deposits are not of syngenetic origin.

7. The S^{32}/S^{34} ratios in sulfide deposits formed by the source bed hypothesis should reflect the nature of the source bed, and exhibit a broad range of S^{32}/S^{34} values. Theoretical considerations (30) suggest that reconcentrated sulfides would have S^{32}/S^{34} ratios equivalent to or slightly greater than the S^{32}/S^{34} ratios in the source bed. If the source bed in the Bathurst area was the sedimentary sulfides, then the deposits should not only be enriched in S^{32} over the source bed ratios, but should also exhibit a broad range of S^{32}/S^{34} values. This is not found. Consequently, it is concluded that the deposits were not reconcentrated from the sedimentary horizons.

8. The sulfide deposits of the Bathurst area all have a very narrow range of S^{32}/S^{34} values. This suggests that the deposits had a homogeneous source. Sulfide deposits that are intimately associated with an intrusive stock, and therefore are thought to have had a magmatic hydrothermal origin, all have a narrow range of S^{32}/S^{34} values. It therefore seems reasonable that well homogenized magmatic hydrothermal solutions are the most logical source for the sulfide deposits.

9. The lead isotope abundance data gives strong independent evidence that the ores came directly from below the crust and therefore are of magmatic hydrothermal origin. However, the relationship between the sulfur and lead isotope ratios is not clear.

10. The massive sulfide deposits can be grouped on the basis of their mean S^{32}/S^{34} ratios. Rather than have a point source with a slight systematic fractionation along the channelways of transport, it appears more reasonable to assume several local sources, closely related in space, but each having characteristics slightly different from each other. In the Bathurst area these local sources possibly are small stocks or cupolas associated with the main granite batholith. The geology of the Bathurst area supports such a model.

ACKNOWLEDGMENTS

This research program was sponsored in part by the United States Atomic Energy Commission—Contract AT (30-1)—1381 M.I.T., the National Science Foundation—Grant 3001, Yale University, and by the Mines Branch, New Brunswick Department of Lands and Mines. The project was supervised by Professors P. M. Hurley, M.I.T., and M. L. Jensen, Yale University. Prof. A. L. McAllister of the University of New Brunswick kindly read and criticized the section on the general geology. The writer, however, assumes responsibility for the views expressed.

I am especially grateful to the following individuals and organizations who contributed samples often at great inconvenience to themselves, and those with whom the geological problems of the Bathurst area were discussed. In particular I wish to thank: Professors G. S. MacKenzie and A. L. McAllister, University of New Brunswick; Dr. R. W. Boyle and Dr. F. Anderson, Geological Survey of Canada; Mr. J. C. Smith, Provincial Geologist, New Brunswick Department of Lands and Mines; Dr. F. Moss, Consolidated Zinc Company of Canada, Limited; Dr. P. Black and Dr. C. J. Sullivan, Kennco Explorations (Canada), Limited; Dr. W. Holyk, Texas Gulf Sulfur Company; Dr. C. G. Cheriton and Dr. T. Zoltai, The Anaconda Company (Canada), Limited; Dr. D. Whitemore, Heath Steele Mines Limited; Dr. A. O. Barker and Mr. O. Hashey, American Metals Climax, Incorporated; Mr. P. Sawyer, Noranda Mines Limited; Dr. W. Little, Consolidated Mining and Smelting of Canada, Limited; Mr. A. B. Baldwin, Boylen Engineering Offices; Dr. G. J. J. Aleva, Nigadoo Mines, Limited; Mr. J. R. Mowatt, Stratmat Limited.

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CAMBRIDGE, MASS.,
Oct. 23, 1959

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Economic Geology
Vol. 55, 1960, pp. 1708–1715

SOME ORE OCCURRENCES OF THE MISSISSIPPI VALLEY TYPE IN EQUATORIAL AFRICA

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ABSTRACT

An area in Equatorial Africa with ore occurrences of the Mississippi Valley Type is described and the characteristics of these occurrences are compared with those given by Dr. E. Ohle for deposits of this type in a previous paper.

In a recent paper entitled "Some Considerations in Determining the Origin of Ore Deposits of the Mississippi Valley Type" Dr. E. L. Ohle (1) summarized the present knowledge of deposits of this type and drew attention to their worldwide distribution. Known occurrences of this type of ore deposit are located in North America, Western and Central Europe and North Africa. The author of the present paper wishes to draw attention to an occurrence of this type of ore deposit in the Lower Congo Region in Equatorial Africa. The formations in which the ore deposits are found occur in a zone stretching from Fougamou in French Equatorial Africa through Cabinda and the Belgian Congo to Quimbango in Angola. Figure 1 is a generalized geological map of the area and the table of formations gives a summarized description of the different formations. They are believed to be Precambrian in age by most geologists but some attribute a Paleozoic age to the formations above the Lower Tillite.

The formations occur in an asymmetric synclinorium which has a NW–SE direction in its northern part and an almost N–S direction in its southern part in Angola. The change in direction occurs approximately at the Congo River. The southwest flank is strongly folded and steeply dipping, locally even overturned. The folds have a NW–SE direction in French Equatorial Africa, the so-called Mayumbien direction. Towards the east this direction is sometimes interrupted by faults and folds with a NE–SW direction. This last direction is locally superimposed upon the Mayumbien direction. This is very noticeable in the eastern flank of the synclinorium where the dips are much more gentle.

Orogenic activity occurred intermittently during deposition of the upper Precambrian(?) but the main activity giving the synclinorium its final shape is post-Inkisi. No intrusive activity except the doleritic sills or lavas in the Lower Tillite occurred. Metamorphism is very weak and does not surpass the formation of sericite flakes.

Copper, lead, and zinc mineralization occurs in some of the formations of the synclinorium. The layers generally mineralized are the top part of the Schisto-Calcaire, notably the massive dolomites and dolomitic limestones,

and some coarse-grained arkoses in the M'Pioka, close to its base. Locally mineralization occurs in the Inkisi. The mineralization is always related to faults and occurs in the favorable layers in the vicinity of the faults or in some places in the faults themselves. The ore deposits are of very local extension and of moderate to high grade. They seem to be concentrated in the area where the direction of the synclinorium changes from NW–SE to N–S. French, Belgian and Portugese geologists seem to agree upon an epigenetic origin for the ore and describe the deposits as typical hydrothermal replacement bodies.

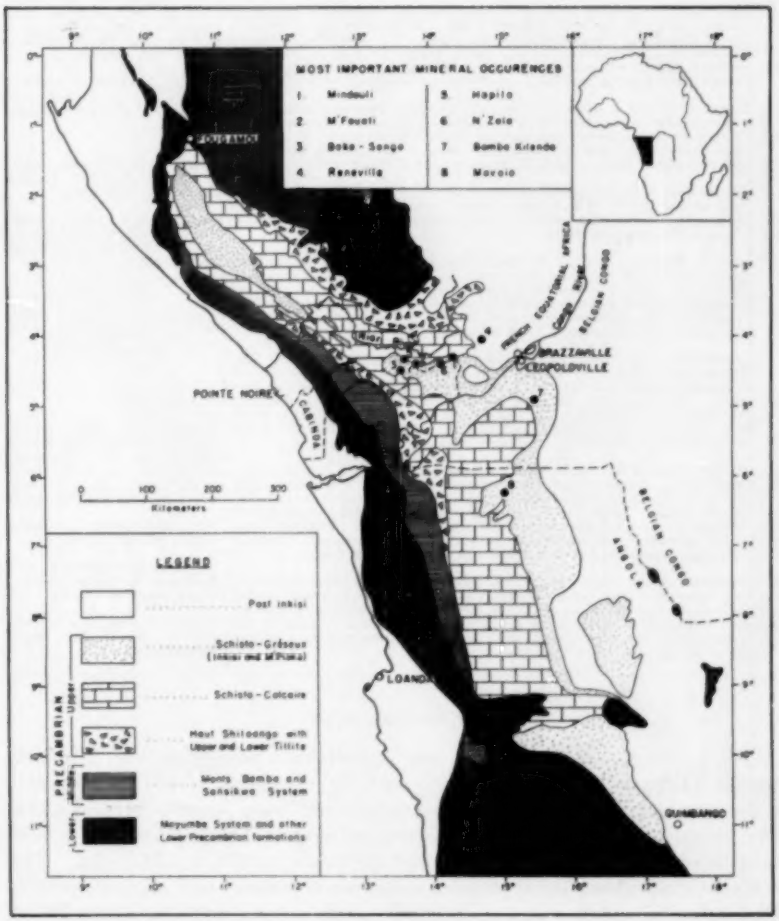

FIG. 1. Geological map of the Lower Congo Region.

Age determinations carried out on galena in the Belgian Congo and French Equatorial Africa indicate an age of 500 to 720 million years for the ore. This agrees with a Precambrian age for the formations in which the ore bodies occur.

TABLE OF FORMATIONS

	Younger formations, mainly Tertiary and Mesozoic	Major unconformity, important orogenic activity forming the synclinorium of the Lower Congo.
Upper Precambrian (?)	*Inkisi:* mostly coarse-grained sandstones, arkoses and conglomerates of reddish color with some argillitic intercalations. The series occurs southwest of Brazzaville in the French Congo where the thickness is 600–700 meters, increasing to about 1,000 meters in the Belgian Congo and Angola.	Slight unconformities have been observed between Inkisi and M'Pioka, probably more activity in French Equatorial Africa than in the Belgian Congo and Angola.
	M'Pioka: fine-grained sandstones, quartzites and argillites of grey-green to grey-blue color, sometimes brown or red. In the lower part of the series some arkosic and conglomeratic layers occur. The base of this series is formed by a conglomerate (locally called 'Brèche du Niari'). The whole series is about 1,000 meters thick. The Inkisi and the M'Pioka are sometimes taken together and then called: Schisto-Gréseux.	Slight unconformity, some pre-M'Pioka faulting and tilting in the Schisto-Calcaire.
	Schisto-Calcaire: a series composed of light-grey massive dolomites and dolomitic limestones, platy dark-grey dolomites, brecciated limestones and dolomites, light colored limestones and marls. At the top locally argillites and sandstones. The series contains some stromatholitic, oolitic and pseudo-oolitic layers. Total thickness around 1,000 meters.	Slight unconformity, some pre-Schisto-Calcaire faulting in the Upper Tillite.
	Upper Tillite: typical glacial conglomerate with intercalations of argillites and varved layers. This formation reaches thicknesses between 125 and 175 meters. This tillite occurs on the eastern as well as on the western flank of the synclinorium.	Erosion and slight angular unconformity of 6–8° between Upper Tillite and underlying formations.
	Louila, Bouenza and Haut-Shiloango: these are local names for the same series which varies strongly in composition from one locality to another. The series consists of quartzitic schists, sandstones, quartzites, arkoses, conglomerates, limestones, sandy limestones, calcarious sandstones and phyllites. The series seems to contain more limestone in the southwest flank of the synclinorium. Total thickness is 800–1,000 meters.	Contact between the Lower Tillite and the overlying formation is gradational.
	Lower Tillite: alternation of conglomerates with fine-grained schists. The schists are locally zonal (varves). The series has the typical appearance of a glacial complex, it occurs only along the southwest flank of the synclinorium. Intercalated in this series are doleritic sills which are probably of the same age as the tillite. In the Belgian Congo the composition of the sills varies between andesitic and basaltic. The total thickness of the series with the intercalated sills varies from 300 to 1,000 meters.	Erosion and slight unconformity between the Lower Tillite and the underlying formations. A diastrophism of uncertain importance occured between the two series.
Middle Precambrian (?)	*Monts Bamba or Sansikwa System:* a series composed of quartzites, phyllites, shales, arkoses, sandstones, conglomerates and some sandy dolomites. Some basic sills occur which are probably related to the dolerites of the Lower Tillite. Some small intrusions of similar material are thought to represent the chimneys of the dolerite sills. Metamorphism of this series is slightly higher than in the overlying formations. The total thickness is estimated to be 1,400 meters in the Belgian Congo.	An unconformity probably occurs within this series.
Lower Precambrian (?)	*Mayumbe System:* under this name all formations west of the synclinorium are included. They consist of highly metamorphic and strongly folded formations such as micaschists, graphitic schists, amphibolites, gneisses and migmatites. Granitic to gabbroic intrusions occur. East of the synclinorium the lower Precambrian is mainly represented by a granite complex, the 'Massif du Chaillu.'	Strong unconformity and difference in metamorphism. Major orogenic activity.
		Probably important unconformity within the lower Precambrian.

ORE OCCURRENCES

As a typical example of the ore deposits in this region, the Mindouli deposit (French Equatorial Africa) will be discussed here. This deposit is the one best known to the author who spent some months here in 1953. The formations occurring in the mineralized area at Mindouli are the uppermost layers of the Schisto-Calcaire and the lower part of the M'Pioka. The Schisto-Calcaire consists of massive dolomitic limestones and platy dolomites. Stromatholitic, oolitic and pseudo-oolitic layers occur commonly in the latter. The M'Pioka starts here with the 'Brèche du Niari,' a conglomerate consist-

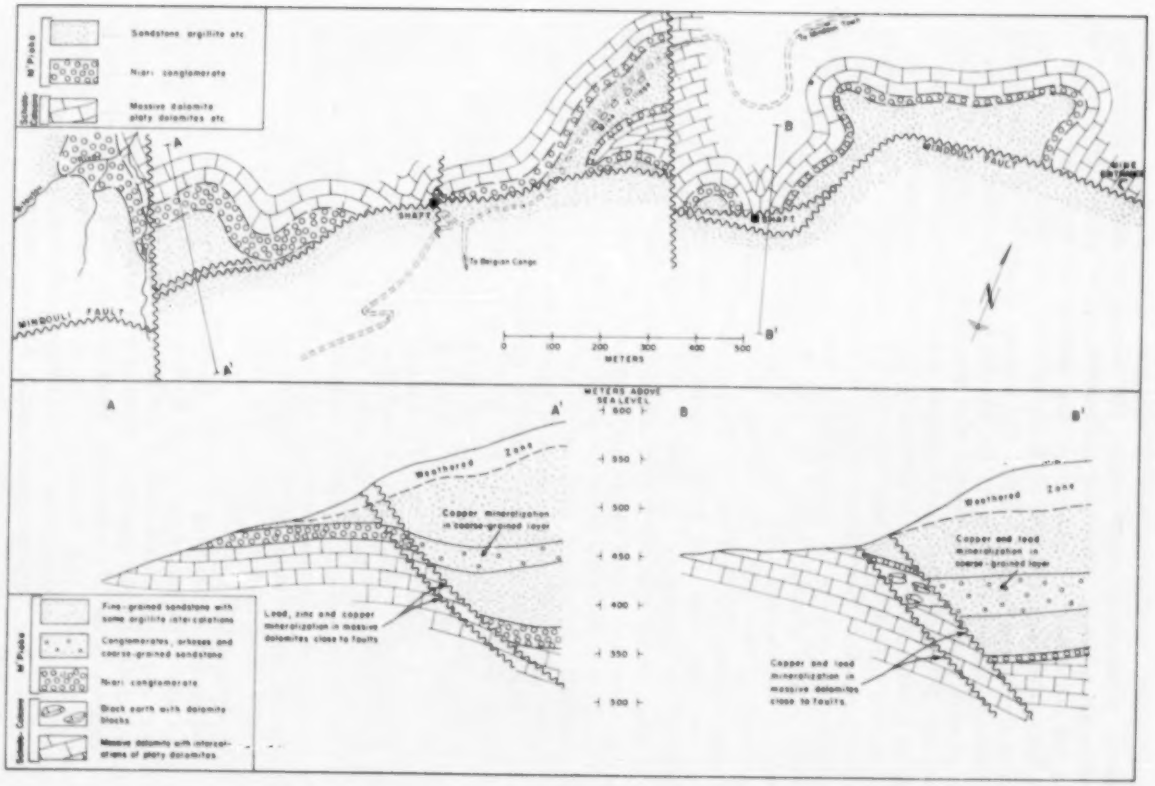

FIG. 2. Mindouli deposit. Geological map and cross-sections.

ing of poorly rounded boulders of limestone, dolomite, chert, quartz, and shale in a calcareous sandy matrix, and varying in thickness from a few centimeters to 30 m. Overlying the conglomerate is a series of gray-green and red sandstones of variable grain-size, arkoses and argillites.

Mineralization in this area is closely related to the Mindouli fault, which strikes approximately N 65° E and dips between 45 and 75° S. The vertical movement varies from 70 ms in the western part of the area to 150 ms in the eastern part. In some places the movement is not restricted to one fault but is spread over several parallel faults. Profiles AA′ and BB′ in Figure 2 indicate this. Cross-faulting in an NNW direction is common.

Surface indications of mineralization are restricted to some chalcocite impregnation and some galena veinlets in massive dolomites and traces of malachite and azurite in coarse-grained sandstones, all in the immediate vicinity of the Mindouli fault. At depth the mineralization occurs in two different surroundings. The first one is in massive dolomites and dolomitic limestones of the upper part of the Schisto-Calcaire, within a distance of approximately 20 ms from the Mindouli fault. The most common minerals are: chalcocite, chalcopyrite, cuprite, malachite and azurite with some dioptase and chrysocolla. Bornite is rare. Galena and sphalerite occur to a lesser degree than the copper minerals, and a little calamine is found. Native silver and native copper are sometimes reported. The mineralization occurs as replacement in the dolomites, which themselves are only slightly recrystallized. Brecciated zones occur and they are generally recemented by calcite, veinlets of calcite and small quartz veins occur in the mineralized zones. The massive dolomites contain in the mineralized sections up to 5% Cu and generally around 0.5 to 1.0% Pb. Locally 1 to 2% Zn occurs.

In some areas the limestone and the dolomite in the fault zone are partly altered into a fine black earthlike material, the so-called 'terre noire'. This black earth averages better than 2% Cu and 1.5% Pb and is an important ore in Mindouli. Little grains of malachite can be seen in the black earth but the amount of visible malachite cannot account for the total copper values, the main copper mineral is probably melaconite. The black earth as well as the mineralized dolomites contain about two ounces of silver per ton of ore. Besides the mineralization in the dolomites and the black earth, mineral veins are locally found along the faults. The veins are up to 30 cm thick and are chiefly composed of chalcocite.

The second surrounding in which mineralization occurs is in a coarse-grained layer in the sandstones. This layer is composed of fine conglomerates, arkoses, and very coarse-grained sandstones with intercalations of fine-grained sandstones and argillites. This layer is between 20 and 30 ms thick and occurs roughly 60 ms above the Niari conglomerate. This layer contains pyrite, chalcopyrite and chalcocite. The chalcopyrite occurs in the upper part of the layer and the chalcocite in the lower part, the two minerals overlap in a narrow zone. Pyrite occurs through the entire layer and locally galena is found. The mineralization in this layer occurs over much larger distances from the Mindouli fault. The average copper values are below 0.5 percent.

The mineral association in the dolomites indicates clearly that the orebody as known thus far falls entirely within the oxidation zone. Almost all minerals are of secondary origin, the only primary minerals are galena, sphalerite and possibly chalcopyrite.

Besides the Mindouli deposit some other important occurrences will be mentioned briefly.

M'Fouati (French Equatorial Africa).—Lead and zinc mineralization occurs in the upper layers of the Schisto-Calcaire along an ENE–WSW fault. The primary minerals are galena and sphalerite but the main ore minerals are cerusite, smithsonite and calamine. As in Mindouli the orebody falls within the oxidation zone. Similar mineralization occurs along the same fault more to the west at *Boko-Songo.* Here some copper minerals occur as a very minor part of the mineralization.

Renéville (French Equatorial Africa).—Here the same type of mineralization occurs as at Mindouli.

Hapilo (French Equatorial Africa).—Lead and zinc sulfides and oxides occur along the contact between the Schisto-Calcaire and the M'Pioka in the vicinity of a NNE fault.

N'Zala (French Equatorial Africa).—Sphalerite, galena and some copper minerals occur in the lower Inkisi along an ENE–WSW fault. NNE cross-faulting has also been observed.

Bamba Kilenda (Belgian Congo).—Mineralization occurs along an approximately E–W fault, dipping to the north. Favorable layers in the vicinity of the fault are mineralized and in places the fault itself. The chief minerals are: chalcocite, sphalerite, galena and pyrite. Minor minerals are: chalcopyrite and bornite. The copper minerals occur mainly in limestones and dolomites directly below the contact with the M'Pioka. Sphalerite, pyrite and galena occur mainly in the coarse-grained layers of the lower M'Pioka.

Mavoio (Angola).—Mineralization occurs in the upper parts of the Schisto-Calcaire along or related to a NNE fault. The chief minerals are: chalcopyrite, bornite and covellite with chalcocite, dioptase, smithsonite, and hematite. In this general area mineralization occurs intermittently over a distance of 6 km along the fault.

Apart from the occurrences mentioned here many more occurrences of copper, lead, and zinc minerals and a little vanadium are known in the general region. At the present time only the deposits at M'Fouati, Mindouli and Mavoio are mined but some of the other deposits will soon go into production.

COMPARISON WITH MISSISSIPPI VALLEY TYPE

A comparison of the characteristics of these ore deposits with those of typical Mississippi Valley Type deposits shows that at least six of the nine conditions mentioned by Dr. Ohle are fulfilled.

1. *Absence of Igneous Rocks that are Potential Sources of the Ore Solutions.*—The only igneous material occurring in the upper and middle Precambrian formations of the synclinorium are the dolerites in the Lower Tillite and they are older than the ore deposits.

2. *Simple Mineralogy.*—The mineralogy of the ore deposits in the Lower Congo Region is far from simple but most minerals are the products of later alteration and oxidation. The primary minerals are galena, sphalerite, and possibly chalcopyrite. Each separate ore deposit varies in its mineralogical composition and even within one deposit this composition may vary from place to place, which is also quite typical for the Mississippi Valley Type deposits. Wallrock alteration is of little importance and amounts only to local recrystallization of the dolomites and limestones.

3. *Low Precious Metal Content.*—In contrast with most Mississippi Valley Type deposits a rather high content of precious metal is reported in at least some of the deposits in the Lower Congo Region. Native silver occurs in Mindouli and Mavoio and the ore in Mindouli contains as much as two ounces of silver per ton of ore.

4. *Occurrence in Limestone or Dolomite.*—This condition is fulfilled in many occurrences as has already been mentioned. Occurrences in coarse-grained sandstones are quite common for Mississippi Valley Type deposits in other localities.

5. *Bedded Replacements and Veins.* The ore deposits in the Lower Congo Region occur in massive dolomites and limestones and in coarse-grained sandstones and arkoses as replacement bodies and in some places as veins along faults.

6. *Most Common Location in Passive Structural Regions.* Much faulting occurs in the mineralized areas but generally the ore-bearing layers are only gently folded.

7. *Shallow Depth.* This condition is doubted by Dr. Ohle, it is true however that all known occurrences in the Lower Congo Region are found at shallow depth or even at the surface but as in many other cases, here also the ore occurrences seem to be controlled principally by the depth at which the favorable formations occur.

8. *Relation to Positive Structures.*—Not enough as yet is known about the structural control of the ore occurrences in the Lower Congo Region. The crystalline basement (Mayumbe System) is very deep in most cases and it is at least very doubtful if the mineralization is related to any structure in this basement. The ore occurrences could be related to other types of positive structures. In Mindouli the mineralization in the dolomites seems to occur in the uplifted part, the mineralization in the sandstone however occurs in the downfaulted part as well as in the unlifted part.

9. *Evidence of Solution Activity.*—Solution activity could have played a role in the formation of the black earth which forms an important ore in Mindouli.

CONCLUSIONS

The occurrence of deposits of the Mississippi Valley Type in the Lower Congo Region is definitely established. Though important discoveries have not yet been made, a number of deposits have been developed and are presently being mined. Considering the fact that this type of deposit has yielded an

important part of the world's lead and zinc, it is certainly worthwhile to study further the potential possibilities of this region.

TORONTO, ONTARIO.
April 3, 1960

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Economic Geology
Vol. 55, 1960, pp. 1716–1738

THE ORIGIN OF THUCHOLITE[1]

HENRY R. HOEKSTRA AND LOUIS H. FUCHS

ABSTRACT

The origin of the organic material, and the mechanism of formation of the organo-uranium complex, in thucholite from the Besner Mine, Parry Sound District, Ontario, have been investigated.

Results indicate that thucholite was formed by the action of aqueous solutions containing organic material, possibly as an oil-in-water emulsion. Uranium, lead, and other relatively soluble oxides were leached from uraninite while aluminum, iron, magnesium, and silica were deposited in the thucholite. The separation of uranium from thorium and the rare earths is believed to have occurred by oxidation of tetravalent uranium to the more soluble hexavalent oxidation state. Oxidation of uranium and the organic fraction of thucholite in an otherwise reducing environment is assumed to be due to the action of radiation decomposition products of water, the hydroxyl radical and/or hydrogen peroxide. Oxidation of the organic material may also be due to subsequent reaction with hexavalent uranium. The liquid and solid hydrocarbons, by virtue of their optical activity, are shown to be of plant or animal origin, rather than polymerization products of methane and other low molecular weight gases. The hydrocarbons are probably not contemporaneous with the organic fraction of thucholite.

INTRODUCTION

ASSOCIATIONS of uranium with organic materials in nature are of many diverse types. Thus uranium is found associated with the organic constituents of black shales, with members of the coal series, with petroleum derivatives, as well as with certain organic materials of unknown origin. Breger and Deul (5) observed that despite these frequent occurrences "the role of organic substances in the geochemical cycle of uranium is not well understood." The problem is particularly difficult in those instances where the origin of the carbonaceous materials themselves is uncertain, i.e., the "carbon leader" of the Witwatersrand, and the "thucholite" or "carburan" of Canada and Russia. As pointed out by Breger and Deul, the lack of information concerning these materials: their origin, mechanism of association, and relationship to each other, has led to the use of a confusing array of names such as *uraniferous asphaltite, hydrocarbon* and *coal*, as well as the *carbon, thucholite*, and *carburan* referred to above.

We have attempted to clarify a portion of this confusing picture by a study of one type of uranium-containing carbonaceous material, the thucholite found at the Besner Mine in the Parry Sound District of Ontario. The term, thucholite, was originally applied by H. V. Ellsworth (9) to a radioactive constituent of a pegmatite in Conger Township of Ontario. The name is

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

derived from the principle constituents of the material: Th, U, C, H, O lite. Almost simultaneously Labuntzov (18) described a radioactive carbonaceous material, carburan, found in pegmatites of northern Karelia, which appears to resemble thucholite in every respect. Spence (26) first described the Besner Mine thucholite, together with its associated liquid and solid hydrocarbons.

In recent years, the name, thucholite, has been applied rather indiscriminately to many types of organo-uranium associations, including hydrothermal vein deposits and sedimentary deposits containing no significant amounts of thorium. Relationships between the varied types of deposits are obscure and no single mechanism can be expected to explain all occurrences. For this reason we are suggesting a mechanism for the formation of thucholite at the Besner Mine. We do believe, however, that the mechanism will be found to have general application to uranium deposits. Analytical data for some thucholites and related organo-uranium complexes are given in Table I.

CLASSIFICATION OF CARBONACEOUS MATERIALS

As reported by Breger and Deul (5), the origin of carbonaceous constituents of organo-uranium associations is frequently in doubt. It thus becomes pertinent to review classification schemes for the naturally occurring organic materials as possible guides in the investigation of substances of unknown origin. One classification method [Hunt, Stewart, and Dickey (17)] is based principally upon the physical properties of the materials, and is illustrated in Figure 1 together with several examples of each group. The carbonaceous shales are not included in this scheme, nor is anthraxolite, a highly metamorphosed asphaltic pyrobitumen. The uranium content of crude oils is generally low (less than 1 ppm) [Erickson, Myers, and Horr (12)]. The bitumens and pyrobitumens may contain higher concentrations of uranium, but only rarely is the uranium content sufficient ($>0.1\%$) to make recovery economical under present conditions. The black shales, both the oil shales and those with coalified plant materials, may contain from 10–100 ppm of uranium. Laboratory tests by Moore (21) have indicated that lignite and sub-bituminous coals are more efficient than other members of the coal series in extracting uranium(VI) from dilute acid solutions. The same sequence is observed in nature, since the ore-grade uranium deposits have been found associated only with these members of the series.

Variations in chemical composition of carbonaceous materials may also be used as a basis for classification. Asphaltic bitumens are composed principally of carbon and hydrogen, together with minor amounts of sulfur, oxygen, nitrogen, and trace quantities of other elements such as nickel and vanadium. These substances, with few exceptions, contain little inorganic material. The nonasphaltic pyrobitumens, or coal series, can be said to contain three principal constituents: carbon, hydrogen, and oxygen. Here again, sulfur and nitrogen are present in minor quantities, but inorganic constituents are generally present to a greater degree.

A detailed discussion of the metamorphosis of petroleum and coal is not warranted here, and the reader is referred to Abraham (1) and Francis (14)

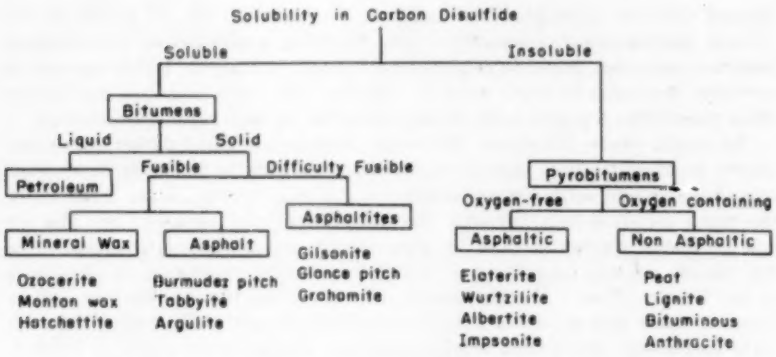

FIG. 1. Classification of carbonaceous materials, from Hunt, Stewart, and Dickey (17).

for this purpose. It will be sufficient to point out some general trends in composition of petroleum and coal during metamorphosis as illustrated by the tri-axial C–H–O plot, Figure 2. It should be noted that the carbon, hydrogen, and oxygen percentages are given in mole per cent rather than the conventional weight percent. Metamorphic processes under the influence of time, heat, and pressure involve principally oxidation and reduction, polymerization, and condensation. For petroleum derivatives, which are composed almost exclusively of hydrocarbons, reduction is unimportant.

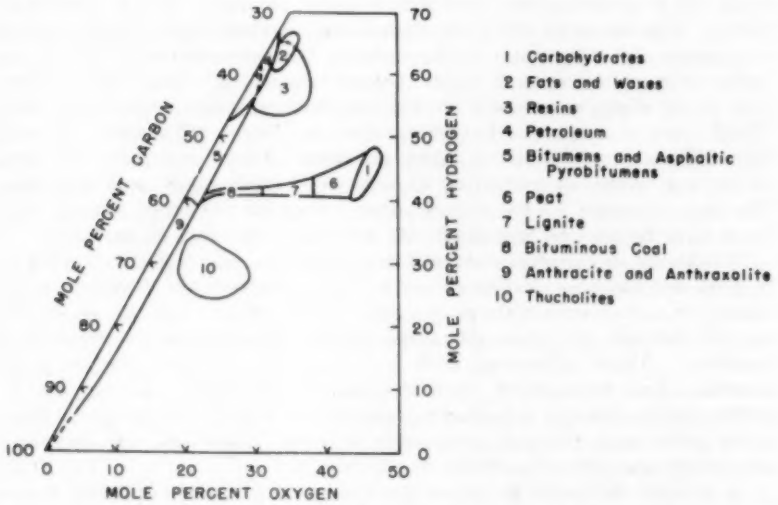

FIG. 2. C–H–O plot showing effects of metamorphism of carbonaceous materials.

From their metamorphosis "line," it is apparent that polymerization and condensation are the principal factors, since liquid and solid bitumens as well as the asphaltic pyrobitumens show little variation in hydrogen-carbon ratio, and all are found in a restricted area of the composition diagram. Only in the later stages of metamorphosis as illustrated by anthraxolite, does oxidation become an important factor. It should be noted, however, that oxidation is accomplished by loss of hydrogen, methane, or other hydrogen-rich low molecular weight hydrocarbons, rather than by the addition of oxygen. The entire process can be considered a reflection of the over-all reducing environment of these materials. Exceptions occur when crude oils and asphalts are exposed to the atmosphere. Here oxidation does involve oxygen addition to some extent.

Evidently two different processes are involved in petroleum metamorphosis, since some of the oldest petroleum deposits are found to have a lower average molecular weight than much younger deposits. As a result, it has been suggested that evolution to crude oils involves a progressive conversion from heavy cyclic hydrocarbons to lighter more paraffinic hydrocarbons in formations of greater age. This requires a process opposite in effect from the customary metamorphic changes, and may be either a reflection of the presence of catalytic agents, of differences in environment, or in starting materials.

The coal series, with its initially high oxygen content, also reflects its reducing environment during metamorphosis. Oxygen is lost rapidly through the peat, lignite, and bituminous stages, while hydrogen loss is minor. The coal "line" given in Figure 2 represents the average coal composition; oxidized coals will fall below the line, whereas the hydrous coals, those rich in resins, fats, and waxes, are found above the average line. In all cases, however, the general pattern is the same—loss of oxygen until three mole percent, or less, remains. At this point, loss of hydrogen becomes important, and the oxygen content remains relatively constant.

Analytical data for thucholite are scarce, but where available, they give a composition outside the range of either the petroleum or coal metamorphosis line. The results given by Figure 2 indicate that thucholites must be classed as oxygen-containing asphaltic pyrobitumens. Data on thucholites were taken from localities numbers 3, 5, 6, 9, and 10 given in Table I. The oxygen analyses are, in general, determined by difference.

MECHANISMS OF ORGANO-URANIUM ASSOCIATION

Of equal importance to an understanding of organo-uranium associations are the mechanisms responsible for the common association of uranium with carbonaceous material. Breger and Deul list three principal mechanisms:

(1) Reduction of soluble uranyl salts to insoluble uranium dioxide by organic matter, or by hydrogen sulfide formed during the decomposition of organic matter.

(2) Chemical adsorption with the formation of an insoluble organo-uranium complex.

TABLE I

ANALYTICAL DATA ON THUCHOLITES AND RELATED CARBONACEOUS MATERIALS

Location	Density	Proximate Analysis				Ultimate Analysis					Ash Analysis			Reference
		H_2O^{110}	Vol.	Fixed C	Ash.	C	H	O	N	S	U_3O_8	ThO_2	PbO	
1. Pied des Monts, Quebec		---40.19---		52.59	7.22						41.78			(27)
2. Karelia, Russia		9.70			9.51	60.96	-19.23-				53.2	----	17	(18)
3. Conger Twp. Ontario	1.78	8.40	17.68	45.86	28.06						5.8	48.48	0.20	(9)
		3.59	38.73	54.20	3.48	67.62	2.84	(23.20)	2.55	0.10				(9)
4. Wallingford, Quebec		13.53	28.70	37.93	19.84						18.2	10.4	----	(10)
5. Besner Mine (pseudomorphic)	1.82	2.00	20.19	50.82	26.86						9.1e			(26)
Ontario (massive)	1.67	1.60	19.96	61.56	16.63						54.4e			(26)
		---26.42----		49.45	24.13	53.35	2.28	(19.63)		1.13	53.09	0.54	1.03	(3)
		---21.04----		54.83	24.13	58.71	1.91	(12.33)	---2.92--					(3)
6. Boliden Mine, Sweden	1.66	1.14			30.15					1.18	39.70	6.20	----	(16)
					23.50	66.54	2.38	--------7.6------						(16)
7. Nicholson Mine, Sask.					5.34						5.2		6.0	(4)
8. Laxey, Isle of Man	1.71				18.67						70.5		0.2	(7)
9. Babrosco, S. Africa	1.83				18.7	42.7	1.7	(13.6)	0.2	3.1	35.8			(7)
	2.29	1.50	15.00	27.90	55.60	27.97					2.91			(19)
10. Blyvooruitzicht, S. Africa		1.9	17.2	64.4	16.5									(19)
	1.66	0.38			16.75	72.68	3.36	6.69	0.14		51.6	1.6	11.2	(19)
11. Geduld, S. Africa	1.64	1.70	18.40	65.70	14.50	72.35					13.1			(19)
12. E. Daggafontein, S. Africa	1.84	1.40	15.60	52.90	30.10	54.94					29.3			(19)
13. Van Dyk, S. Africa	1.62	1.00	17.90	61.90	19.20	68.78					9.9			(19)
14. Placerville, Colorado					3.72	87.34	4.28	--------4.66------			31.7			(6)
15. Temple Mt., Utah					12.85	68.86	4.21	8.27	0.24	5.60	27.1			(6)
16. Gila County, Arizona						88*	4.5	--------7.5------						(6)

*Analysis calculated on an ash-free basis.

(3) Physical adsorption as a result of surface activity of the organic matter.

In each instance uranium, as the uranyl ion, is assumed to have been present in solution from which precipitation occurred into a sedimentary carbonaceous formation. All three mechanisms involve transportation of uranium to the organic matter. Thucholite, of the type found at the Besner Mine, requires a different mechanism since tetravalent uranium, as uraninite, is apparently replaced by the organo-uranium complex.

A mechanism has been suggested to account for thucholite and certain other organo-uranium complexes, i.e., polymerization of liquid or gaseous hydrocarbons by radioactivity. This mechanism was first postulated by Spence to account for the Besner Mine thucholite-oil association. He suggested that oil, derived possibly from overlying sedimentary strata, had been polymerized to form the coal-like material. Others [Vernadsky (30), Grip and Odman (16), Davidson and Bowie (7)] have suggested that natural gases such as methane, acetylene, and carbon oxides, rather than oil, are the raw materials for the formation of thucholite. The existence of methane in the natural gases from mines containing thucholite, together with experimental evidence for radiation polymerization of methane by Lind (20) are cited as proof of the theory. Davidson and Bowie have pointed out that polymerization of hydrocarbons is not the entire answer, since solution and replacement of uraninite by the organic complex are also to be explained. They suggest that "since uranium oxide is relatively soluble in various organic liquids, particularly in the presence of mineral acids, . . . the fluid (hydrocarbon) phase may well be able to remove part of the uranium in solution."

Breger and Deul (5), however, minimize the importance of radioactive polymerization of gases, and reiterate the suggestion of Spence (26) and of Quirke (25) that the organic material of the Besner Mine was derived from oil that seeped downward from sedimentary strata which have since been eroded away.

PROPERTIES OF THUCHOLITE

The thucholite from Conger Township was described by Ellsworth (9) as a black mineral with conchoidal fracture, no cleavage, brittle, hardness 3–4, with a specific gravity of 1.78. It is insoluble in hydrochloric acid, except for a partial leaching of the inorganic constituents, and is decomposed slowly by hot concentrated nitric acid. Analysis gave an ash content of about 25 percent, containing 5.8 percent U_3O_8 and 48.5 percent ThO_2.

The Besner Mine thucholite, reported by Spence (26) is quite similar to the Conger thucholite. It was found in a pegmatite dike cutting Archean biotite gneiss. Most of the thucholite occurred near the dike walls, at or near the surface. Spence listed five forms of thucholite but these may be classed as variations of two main types: pseudomorphic (after uraninite), and massive (filling cracks and crevices). Variations in the composition of thucholite are illustrated by the results of proximate analysis, density, and total activity reported by Spence (Table I) for the pseudomorphic and

massive forms. The ash of individual samples is not homogeneous as evidenced by variations in color and the existence of identifiable crystals of nonradioactive compounds. Minerals listed as being associated with thucholite in the dike are allanite, beryl, biotite, cyrtolite, garnet, martite, pyrorthite, titanite, and uraninite. Of added interest was the presence of an oil, and small blebs of solid asphalt-like material, both occurring in cavities along two fracture zones crossing the dike. These zones are made up of brecciated feldspar and quartz cemented by calcite, quartz and pyrite. The crevices were covered with a film of viscous oil and pea-like balls of hardened oil—some of which were tacky, others hard and brittle. Analysis of the hardened oil (on an ash-free basis) gave: carbon 86.76 percent, hydrogen 12.16 percent; H/C = 1.68.

Barthauer, Rulfs and Pearce (3) studied Besner thucholite from a standpoint of its thermal decomposition in air and in vacuum. They found the volatile matter from thucholite to consist primarily of water and carbon dioxide, with lesser amounts of methane, carbon monoxide, and hydrogen. No higher hydrocarbons were found. A chemical analysis of the ash was also reported.

EXPERIMENTAL PROCEDURE AND RESULTS

Our samples were a portion of Spence's collection and were obtained through the Harvard Mineralogical Museum. Since no possibility existed for a field observation at the Besner Mine, we have relied on the description given by Spence (26). Our samples were divided into six groups on the basis of a preliminary visual inspection.

1. Massive thucholite with minor quantities of adhering associated minerals.
2. Pseudomorphic thucholite as cubes.
3. Uraninite partially replaced by thucholite.
4. Feldspar containing small thucholite pseudomorphs, as well as a few bits of massive and vein type thucholite. Included in this group is the black mineral present in fan-shaped aggregates and tentatively listed as pyrorthite by Spence.
5. A large number of thucholite "chip" samples of varying degrees of purity.
6. Samples of the fracture zone containing oil-soaked rock, gummy and hard carbonaceous pellets.

Relation Between Organic Matter of Thucholite and Oil

Spence, in his discussion of the oil-thucholite relationship, reported that "thucholite . . . was found . . . close to the oil zone but not visibly connected with it. . . . It seems that the thucholite is not disseminated irregularly throughout the dyke-mass, but that it tends to occur in proximity to the oil zones."

A careful study of our specimens under the microscope revealed, in agreement with Spence's observation, no evidence of direct physical connection

between the oil and thucholite. Only one specimen was found that contained both thucholite and the hardened oil. Here, too, the demarcation between the two forms was sharp and distinct, rather than a gradual change from the oil to thucholite.

Further evidence for the separation of the two organic materials is provided by the associated minerals. As reported by Spence, the channels containing oil consist of fracture zones with angular fragments of feldspar cemented by calcite, quartz, pyrite, and marcasite. No calcite was found associated with thucholite and only traces of pyrite and marcasite were identified.

Density of Thucholite and Associated Organic Matter

Spence reported a density range of 1.57 to 1.67 for massive Besner thucholite and 1.61 to 2.00 for pseudomorphic crystals, and Barthauer reported a density of 1.86, without indicating the type of thucholite. The density of a number of thucholite samples, which had been carefully freed of impurities, was determined pycnometrically, and found to vary between 1.46 and 2.26. Individual samples of approximate equal density showed wide variation in ash content. Combination with analytical and X-ray data indicated that wide variations in thucholite composition exist, and residual fragments of the original uraninite are commonly present. These results are in agreement with earlier observations by Spence and by Davidson and Bowie. Extrapolation of the thucholite density to zero ash content gives an approximate density of 1.40 for ash-free carbonaceous material.

The density of one of the hard brittle organic pellets was found to be 1.10 as compared with a range of 1.000 to 1.086 reported by Spence for both the hard and soft material. The slightly higher density of our pellet is undoubtedly due to its longer exposure to the atmosphere.

Analysis of Thucholite

Ash.—Analytical data on thucholite ash is relatively meager. Ellsworth listed one analysis on Conger thucholite, but the only data on the Besner material has been reported by Barthauer. Confirmation of the varied composition of thucholite afforded by our preliminary density and X-ray results indicated the necessity for an extensive investigation of ash composition. It was hoped to establish whether variations in composition are random or whether a definite pattern would evolve which would be of assistance in the determination of a mechanism of thucholite formation. A complete chemical analysis is not only laborious and time-consuming, but requires relatively large samples. Results obtained from the combination of a number of small, relatively pure thucholite samples would represent only an average composition, which might have little significance relative to any one of the specimens making up the combined sample. Spectrographic techniques have a great advantage over conventional wet procedures in that only milligram quantities of sample are required for an analysis that includes approximately fifty metals. The principal disadvantage of the method is,

of course, its lack of precision. However, by proper technique the copper spark method has been shown to give results accurate within a factor of two (15). On the assumption that its advantages outweight the disadvantages, we have used this technique to study the variations in thucholite composition. More than one hundred samples of thucholite, uraninite, and associated minerals were analyzed spectrographically. An attempt was made to select samples of as many different forms of thucholite as possible—massive and pseudomorphic, high and low density, thucholite associated with uraninite, with "pyrorthite," in veins, etc., in order to obtain as complete a spectrum of thucholite composition as possible. Analyses of associated minerals were obtained for identification purposes and to trace their role, if any, in the formation of thucholite.

Samples were prepared for analysis by ashing in air to constant weight at 500° C; in some instances a preliminary water analysis was obtained at 110° C. The average water content of sixteen samples was 2.40 percent, the range being 1.26 to 4.46 percent. The color of the ash obtained by ignition at 500° C fell into three groups: (1) green to yellow, (2) tan or buff, and (3) orange to rust. These were shown by subsequent analysis to be correlated with (1) high uranium, (2) high thorium, and (3) high iron contents. The samples of thucholite ash were then inspected under 10 × magnification. If more than one phase was visible (as evidenced by color variation, crystal form, luster, etc.) the components were separated as cleanly as possible and separate analyses obtained on each fraction. Since only milligram quantities were required, components representing less than 1 percent of a thucholite ash could be separated and identified.

Results of the numerous spectrographic analyses of thucholite ash and its associated minerals indicated that the samples could conveniently be divided into five groups: (1) uraninites, (2) uranium thucholites, (3) thorium thucholites, (4) cerium-earth thucholites, and (5) associated minerals.

Figure 3 shows three views of a uraninite which had been partially converted to thucholite. Figure 3A shows a section of the original specimen; Figure 3B is an autoradiograph of the section; and Figure 3C illustrates its appearance after ignition to constant weight in air at 500° C. The dark portions of the autoradiograph indicate high activity and consist principally of unchanged uraninite. The numerous solution channels are particularly evident in B and C. The thucholite that fills the channels and encloses the uraninite on three sides is a uranium thucholite, but its relatively low density and ash content is reflected in the weak activity shown by the radiograph and the appearance of the ash.

Five of the best uraninite samples have been averaged in Table II and compared with a chemical analysis reported by Ellsworth (11). A number of additional uraninite analyses were obtained from less pure samples, but none indicated the presence of a uraninite with radically different composition. Thus, the starting material for thucholite formation can be considered to have a relatively constant composition.

Two types of thucholite were found most frequently: those with a

uranium-thorium ratio greater than four (uranium thucholites), and those with a ratio of about 0.25 (thorium thucholites). The former group had a total uranium plus thorium content in the ash approaching that of uraninite, while the latter ranged from a maximum of about 30 percent to a minimum of approximately five percent. No significant change in the uranium-thorium

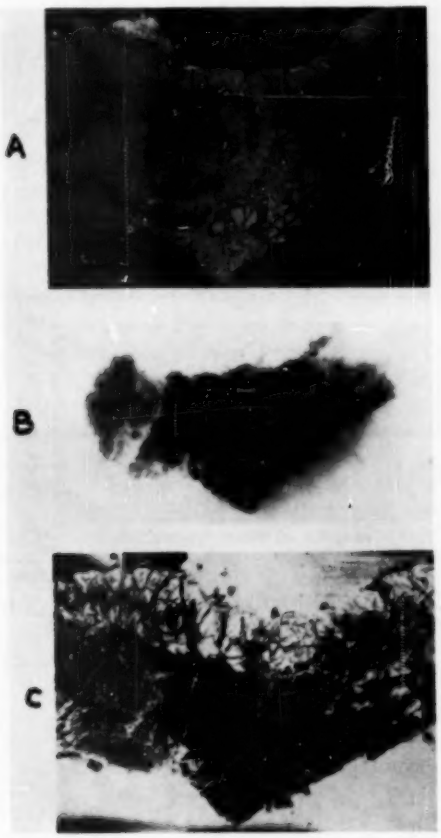

FIG. 3. Section of uraninite partially converted to thucholite. Magnification 2.5 ×. A. Original specimen. B. Autoradiograph. C. Ignited in air at 500° C.

ratio occurred over this composition range. Less than ten percent of the thucholites analyzed were found to have an intermediate uranium-thorium ratio. Analytical results on thirty samples of these thucholite types are summarized in Table III. In general, massive thucholites are found in the uranium group, whereas the pseudomorphic, or crystalline, thucholites are

TABLE II

ANALYSIS OF HESNER URANINITE

Oxide	Composition Range Lower	Upper	Average	Ellsworth Analysis
Al_2O_3	<0.1 %	0.2 %	0.1 %	0.17 %
BaO	<0.02	0.08	0.02	
CaO	1.5	2.5	2	2.69
CeO_2	<0.1	0.4	0.25	1.47*
Dy_2O_3	0.1	0.5	0.3	
Er_2O_3	0.1	0.2	0.15	
Fe_2O_3	0.1	0.6	0.3	0.88
Gd_2O_3	0.1	0.4	0.25	
K_2O	0.05	0.05	0.05	
La_2O_3	<0.02	0.1	0.035	
MgO	<0.01	0.03	<0.03	0.03
MnO	0.08	0.3	0.1	0.02
Na_2O	0.1	0.5	0.25	
Nd_2O_3	0.2	0.5	0.35	
PbO	4.5	13	9.5	8.66
Sm_2O_3	0.1	0.25	0.2	
SrO	0.007	0.07	0.035	
ThO_2	1	3	2	1.78
UO_2	>50	>50	80†	77.5
V_2O_3	<0.08	<0.08	<0.08	
Y_2O_3	0.6	2.5	1.5	
Yb_2O_3	0.3	0.6	0.35	1.48‡
SiO_2				1.36

*Cerium earths †By difference ‡Ytterbium earths

TABLE III

ANALYSIS OF HESNER THUCHOLITES

Oxide	Uranium Thucholites Composition Range Lower	Upper	Average	Thorium Thucholites Composition Range Lower	Upper	Average	Intermediate Average
Al_2O_3	0.5 %	5 %	2 %	5 %	15 %	10 %	9 %
BaO	<0.01	0.08	0.03	<0.01	0.03	0.01	0.1
CaO	0.5	2.5	1.5	0.6	3	1.3	1.5
CeO_2	<0.1	0.8	0.4	0.3	7	2.5	0.7
Dy_2O_3	1	2	1.5	0.5	2.5	1.2	1.1
Er_2O_3	0.5	1.5	0.9	0.3	1	0.8	0.9
Fe_2O_3	0.15	6	1.2	3	20	10	11
Gd_2O_3	0.5	1	0.7	0.3	1	0.7	0.7
K_2O	0.05	1	0.4	0.01	0.1	0.06	0.8
La_2O_3	<0.02	0.1	0.03	0.05	1.5	0.6	0.2
MgO	0.015	1.2	0.3	1.5	8	5.5	1.7
MnO	0.05	0.2	0.1	0.005	0.1	0.05	0.3
Na_2O	0.06	1	0.6	<0.05	0.5	0.1	0.8
Nd_2O_3	0.2	1	0.8	0.3	4	1.4	0.5
PbO	2	4	2.6	0.1	0.5	0.3	1.9
Sm_2O_3	0.2	1	0.5	<0.1	0.4	0.2	0.3
SrO	0.02	0.15	0.08	0.01	0.4	0.09	0.08
ThO_2	2	9	6.2	10	35	19	13.5
UO_2	50	>50	60*	2	9	4.5	30
V_2O_3	0.06	3	0.6	0.6	4	2	0.7
Y_2O_3	4	12	7.2	4	10	6	7
Yb_2O_3	0.5	3.5	1.5	0.8	2.5	1.3	1.3
SiO_2			12.4			21.9	21.3

*By difference

found to be thorium thucholites, although a few exceptions were found. As a rule, samples containing unreacted uraninite were uranium thucholites, although several contained portions whose composition coincided with the intermediate group. No traces of residual uraninite were found in any thorium thucholite.

Cerium-earth thucholites were found infrequently and appeared to be related to the thorium thucholites. Fractions were isolated containing as high as 40 percent cerium oxide; others contained less, approaching the regular thorium thucholites in composition. Several representative analyses of this group are given in Table IV. Analyses of the fan-shaped aggregates that Spence referred to as "pyrorthite, largely converted to chlorite," are also included. The first of these appeared to be the least altered, the last the most completely altered. Among the associated minerals identified were feldspar, biotite, cyrtolite, brookite and garnet.

The spectrographic analyses were supplemented by separate analyses for silica and sulfur on some of the samples. Silica analyses were obtained using the standard hydrofluoric-sulfuric acid procedure. The results are included in Table V and indicate an increase of silica in the order uranium < intermediate < thorium and cerium-earth thucholite.

A number of thucholite samples were analyzed for sulfur before ashing. The results varied between 0.52 and 1.32 percent sulfur with an average value of 0.85 percent.

Organic Fraction.—Portions of several thucholite samples that had been dried at 110° C were analyzed chemically for carbon and hydrogen. In addition, a single analysis was obtained of a hard pellet from the oil zone. The results, Table VI, indicate a slow and relatively constant H/C ratio for the thucholites, which evidences no direct correlation with the total radioactivity (U + Th) of the sample. The oxygen content obtained by difference, is in agreement with earlier analyses on thucholites (Fig. 2) and emphasizes the oxidized nature of this material. The oxygen content is much higher than is found in anthraxolite or in any of the other metamorphic products of petroleum.

Uranium Oxidation State in Thucholite.—The oxidation state of uranium present in thucholite was investigated by solution in hydrochloric acid. From Ellsworth's data (9) it would appear that most of the uranium can be leached from thucholite by boiling in 3 *N* HCl. Our experiments carried out in a nitrogen atmosphere showed that about half the uranium was soluble, predominantly as UO_2^{++}. Repetition of the experiment with concentrated acid in an evacuated tube found almost all of the uranium in solution—in the tetravalent oxidation state. In order to determine the significance of this result relative to the uranium oxidation state in the thucholite, a test was made of the reducing power of the carbonaceous material under the extraction conditions. A solution of UO_2Cl_2 in concentrated acid was heated at 100° C for 60 hr. At the end of this period the uranium had been completely reduced to U(IV). The experiments serve to prove that the uranium oxidation state in thucholite cannot be determined in this manner.

TABLE IV

ANALYSIS OF CERIUM THUCHOLITE AND CHLORITE

Oxide	Cerium Thucholite #1	#2	#3	"Pyrorthite"--Chlorite #1	#2	#3
Al_2O_3	5 %	4 %	7 %	30 %	20 %	15 %
CaO	30	25	6	0.7	0.1	0.3
CeO_2	40	40	10	<0.1	<0.1	<0.1
Dy_2O_3	0.7	0.8	1	<0.1	<0.1	<0.1
Er_2O_3	0.3	0.3	0.4	<0.02	<0.02	<0.02
Fe_2O_3	2.5	2	6	25	15	8
Gd_2O_3	2	1.5	0.3	<0.1	<0.1	<0.1
La_2O_3	12	6	3	<0.02	<0.02	<0.02
MgO	2	0.6	2	30	20	25
Nd_2O_3	10	15	6	<0.1	<0.1	<0.1
PbO	0.04	0.3	0.3	0.15	0.1	0.03
Sm_2O_3	4	2	0.3	<0.2	<0.2	<0.2
ThO_2	1	7	20	<0.2	<0.2	<0.2
UO_2	0.3	3.5	4.5	<0.4	0.5	<0.4
V_2O_3	0.6	0.6	2.5	0.1	0.04	<0.04
Y_2O_3	6	4	4	0.003	0.05	0.05
Yb_2O_3	0.4	0.3	1	<0.002	<0.002	<0.002

TABLE V

SILICA CONTENT OF BESNER THUCHOLITES

Thucholite type	% Ash	$\%SiO_2$ in ash	$\%SiO_2$ in thucholite
Uranium	7.5	6.7	0.5
Intermediate	12.1	16.5	2.0
Thorium	15.5	16.9	2.6
Uranium	23.9	16.6	4.0
Intermediate	34.7	15.5	5.4
Thorium	28.4	22.7	6.5
Cerium-earth	30.6	22.1	6.8
Thorium	65.2	16.7	10.9
Thorium	46.0	26.1	12.0
Thorium	56.4	21.5	12.1

TABLE VI

CARBON-HYDROGEN ANALYSES OF BESNER THUCHOLITE AND CARBONACEOUS PELLET

Thucholite type	Wt % ash	Wt % C	Wt % H	Wt % N	H/C molar ratio
Uranium	12.80	75.42	3.25	< 0.1	0.52
Uranium	15.10	69.30	2.94		0.51
Thorium	44.61	42.97	1.96		0.55
Thorium	32.47	51.72	2.12		0.49
Thorium	17.11	65.64	2.11		0.39
Pellet	0	82.7	11.0		1.60

X-Ray Studies on Thucholite

X-ray diffraction photographs on the first thucholite samples were obtained from both the original material and the ash. In most instances, the structure obtained from the ash was identical with that found in the original sample. This fact, together with the inability to recognize fractions of different composition in the original sample, led to the investigation of only the ash in later samples.

Uraninite thucholites almost invariably contained traces of residual uraninite, even though none was visible under 30 × magnification. The uraninite could be differentiated from "dissolved" (or amorphous) uranium oxide by the fact that its fluorite structure is retained during the ashing process, while the amorphous material is converted to an oxide whose defect hexagonal structure indicates a composition intermediate between α UO_2 and U_3O_8. Retention of the cubic structure upon ignition in air at 500° C has been observed for uraninites from many localities. In this respect, they differ from synthetic uranium dioxide which is converted to U_3O_8. The reason for this difference is not well understood, but may be due to the presence of small quantities of thorium, rare earth, and possibly alkaline earth oxides dissolved in the uranium dioxide crystal which stabilize the fluorite structure. Alternatively, the apparent stability may be due to the relatively small surface area and consequently diminished reactivity of the uraninites.

The majority of thorium thucholites had the tetragonal uranothorite, $(Th,U)SiO_4$, structure—both in the original material and in the ash. Only one uranium thucholite was found to have this structure; it should, therefore, be classed as coffinite (28). Some of the associated minerals identified include cyrtolite, brookite, and garnet.

Infrared Studies on Thucholite

Infrared absorption studies have become useful in the identification of many types of bonding in organic and in inorganic compounds. We have used this technique to study thucholite, its inorganic ash, and the associated oil from the Besner Mine. Spectra were obtained on a Perkin-Elmer Model 21 recording infrared spectrophotometer, using a NaCl prism. Two methods were used to prepare samples. The oil was analyzed as a thin film between NaCl plates. Solid samples were analyzed by the potassium bromide disk technique. Infrared quality potassium bromide containing 1 percent of the solid being analyzed was pulverized thoroughly in an agate mortar or in a Wigl-bug amalgamator before being pressed into a disk at a pressure of 5,700 psi.

Spectra in the 2 to 15 μ range were obtained for several thucholite samples. Only one of those tested contained any trace of identifiable C–H bonds (hydrogen stretching 3.45–3.55 microns; hydrogen bending 6.85 and 7.25 microns). The remaining samples showed only indefinite weak absorption maxima in the C=O and C=C regions (5.88 and 6.23 microns). Confirma-

tion for the absence of a volatile organic component in thucholite was provided by attempts to extract and vacuum distill oil from thucholite. Approximately 800 grams of thucholite which had been ground to a fine powder in a ball mill, gave only 0.05 cc of a dark oil that exhibited a complex spectrum. This small quantity could easily have resulted from contamination during storage and handling, and very little significance can be attached to the spectrum.

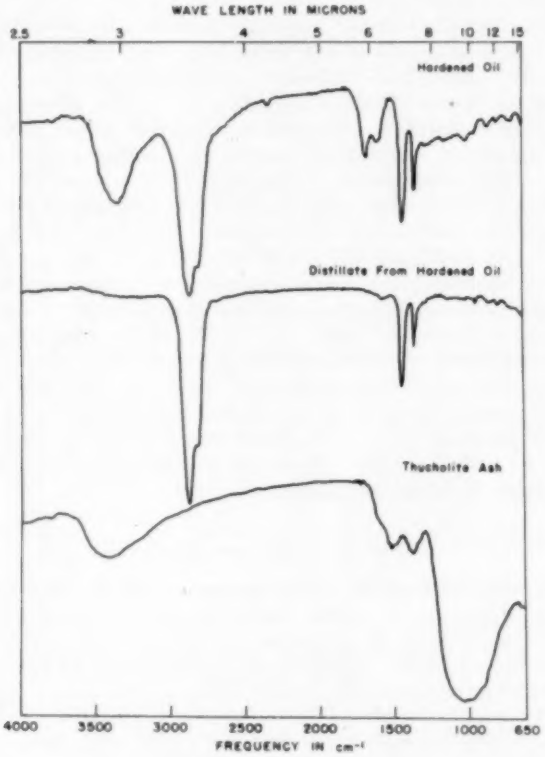

FIG. 4. Infrared transmission spectra of solidified oil pellets, distillate from the pellets, and thucholite ash.

The solidified oil pellets gave the characteristic spectrum of aliphatic hydrocarbons, with minor amounts of C=O and C=C absorptions. The oil distilled from the pellets showed still less of the latter two functional groups, while oil further purified by repeated treatment with activated alumina gave a spectrum very closely resembling a paraffinic oil. Representative spectra are included in Figure 4.

Optical Activity of Oil

The presence or absence of optical activity in the oil associated with Besner thucholite could provide a valuable clue to its origin. Naturally occurring oils invariably show some optical activity, and oils produced by polymerization of gaseous hydrocarbons should be optically inactive.

All of the gummy oil was consolidated by solution in carbon tetrachloride. To this was added oil distilled in vacuum from the resin-like pellets. The dark amber viscous oil obtained in this manner was further purified by treatment with activated alumina. These purification steps have been shown by Fenske et al. (13) not to affect the optical activity of oils. The final product was 0.7 cc of a light amber-colored viscous oil having a refractive index of 1.51. This was diluted to a 2.7 cc with carbon tetrachloride, poured into a 10-cm long semimicro polarimeter tube, and its optical activity measured on a Rudolph Model No. 80 Polarimeter using a mercury light and a Corning absorption filter No. 3480 to isolate the mercury yellow line at 5780 A. The oil-carbon tetrachloride solution was found to have a + 0.073° rotation; a blank run using only the solvent gave an average reading of 0.001°. The calculated specific rotation is + 0.31 degrees/decimeter, which may be compared with the value obtained by Fenske for the most active fraction of Pennsylvania oil (+ 0.25).

DISCUSSION

Two important problems concerning thucholite have been shown to be (1) origin of the carbonaceous material, and (2) the mechanism responsible for the organic-uranium association.

The presence of oil in the pegmatite suggests a convenient and plausible source for the organic fraction of Besner thucholite. As pointed out in the preceding section, however, there is no physical evidence for any direct relationship between the oil and thucholite. In addition, the presence of less than 0.01 percent volatile hydrocarbons, other than methane formed during thermal decomposition, in thucholite, and less than 0.01 percent ash in the oil suggests that thucholite and the oil are not fractions of the same material.

Although the oil has been shown to be of plant or animal origin, the evidence gathered by our investigation is insufficient for a similar statement regarding the organic fraction of thucholite. However, the fact that the oil found its way into the pegmatite along the fracture zone does lend weight to the belief that a similar earlier migration of oil was responsible for the thucholite organic fraction. The absence of volatile hydrocarbons in thucholite, together with relatively consistent ages (250–400 million years) obtained from lead-uranium ratios and isotopic lead studies by Muench (22), and Nier, Thompson, and Murphey (24) makes it highly improbable that thucholite was being actively formed at the time the samples were taken from the pegmatite.

Our suggested mechanism of thucholite formation from uraninite is derived from the experimental results together with a consideration of certain aspects of uranium chemistry. On the basis of our analytical results, it appears that the variations in Besner thucholite composition are not random,

but have a definite pattern. Our postulated mechanism is based on an assumption that the uraninite composition reported by Ellsworth (9) and given by Table II represents the primary mineral for the Besner thucholites. This assumption appears justified, since the search for other uranium and thorium minerals proved unsuccessful, with the exception of evidence for the presence of minor amounts of allanite in the cerium-earth thucholites. Allanite and uraninite were also the only radioactive minerals reported by Spence. Its poor resistance to weathering may explain the scarcity of residual allanite in our specimens.

The straightforward replacement of uraninite ($D \cong 10$) by thucholite ($D \cong 1.7$, 20 % ash) would require approximately a thirty-fold increase in volume. This factor presumably would account for thucholite filling cracks and crevices in the surrounding pegmatite, as well as the space occupied by the original uraninite. A consideration of thucholite composition, however, reveals that the replacement process involves more than dissolution of uraninite and reprecipitation of the constituents in the organic complex. Thus, thucholite always exhibits a lower uranium-to-thorium ratio than does the parent uraninite. In addition, uraninite of relatively uniform composition is converted to thucholite with widely varying composition. These facts indicate that a selective replacement process involving a true solution of uraninite rather than mere physical break-up is involved. It is also evident that lead has been removed during this process, since the calculated thucholite age is approximately one-third that of the parent uraninite age, 800 million years (23).

We have calculated the variation in uranium plus lead-to-thorium content (Fig. 5) as a function of the percentage of uranium and lead oxides removed from the parent uraninite. From this plot, which assumes that lead is removed as rapidly as the uranium is dissolved, it becomes apparent that the product remains a uranium thucholite (by our definition) until approximately 90 percent of the uranium has been removed, an intermediate thucholite between 90 and 99 percent uranium removal, and finally a thorium thucholite. This process explains the scarcity of samples in the intermediate thucholite composition range. Since the uranium-to-thorium ratio of the thorium thucholites is relatively constant, this ratio apparently represents the endpoint of the solution process. The remaining uranium evidently becomes incorporated in the thorite lattice that replaces the uraninite, and is no longer easily susceptible to oxidation and solution.

In order to make a comparison of the observed and calculated percentages of the remaining constituents of uraninite in its conversion to thucholite, we have assumed that the conversion of uraninite to uranium thucholite occurred by the dissolution of 75 percent of the uranium and all of the lead. It is possible that a portion of the lead present at the time of thucholite formation was retained, but this is unimportant to the postulated mechanism. This process represents a loss of seven-tenths of the original uraninite. Recalculation of the remaining materials to 100 percent (Table VII, column 3) permits comparison with the observed average composition of uranium thucholites.

A similar calculation was made for the thorium thucholites by assuming that 99 percent of the original uranium and all of the lead was removed. Seven-eighths of the original uraninite is removed by this process. A comparison of observed and calculated compositions is given in columns 4 and 5.

A study of the observed and calculated thucholite composition reveals that our proposal represents an oversimplification of the actual process. Certain of the constituents, namely aluminum, iron, magnesium, vanadium, and

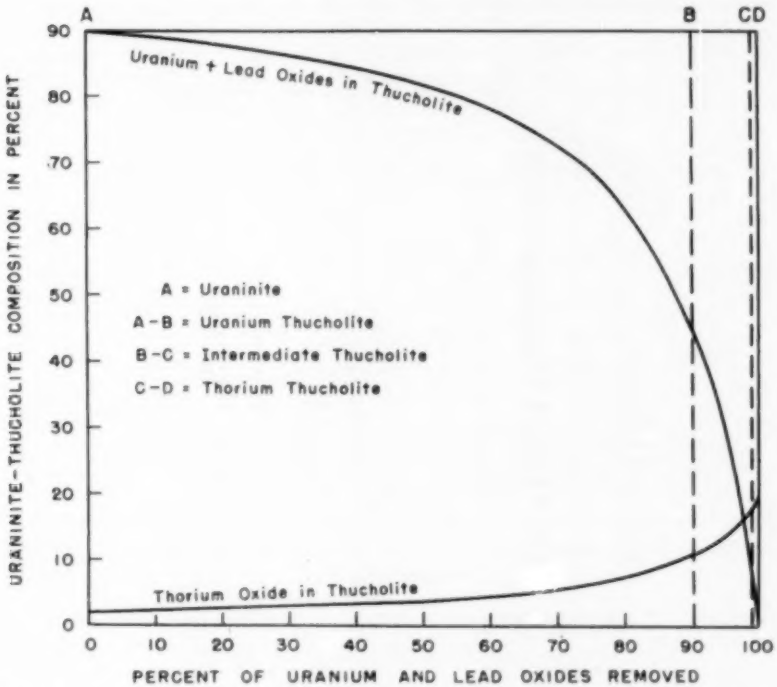

FIG. 5. Calculated composition of uraninite or thucholite ash as a function of loss of uranium and lead oxides.

silica, are consistently present in greater than calculated quantities. With the exception of vanadium, these represent the principal constituents of the dark chlorite mineral (Table IV) so closely associated with thucholite. It seems likely that the excess of these oxides over the calculated thucholite composition represents contamination of the thucholite by chlorite. This premise is verified by the observation that thucholite ash commonly contains traces of a flaky dark green mineral. In several instances sufficient material was isolated for analysis, and found to be chlorite. The reason for the presence

of excess vanadium is less easily explained. It may represent one of the less soluble components of uraninite, or possibly be derived from the oil that represents the major constituent of thucholite.

Some additional information concerning the solution process is obtained by plotting individual samples rather than combining them into three major groups. It must be borne in mind that the accuracy claimed for the spectrographic analyses is only a factor of two. As a result, only broad generalizations can be made concerning them. In Figure 6 are plotted the U, Th, Fe, Al and rare earth concentrations of about 30 samples drawn on a smoothed

TABLE VII

COMPARISON OF THUCHOLITE ASH COMPOSITION

Oxide	Uranium Thucholites		Thorium Thucholites	
	Observed	Calculated*	Observed	Calculated**
Al_2O_3	2.0 %	0.35 %	10 %	0.9 %
BaO	0.03	0.07	0.01	0.2
CaO	1.5	7	1.3	18
CeO_2	0.4	0.8	2.5	2
Dy_2O_3	1.5	1	1.2	3
Er_2O_3	0.9	0.35	0.8	0.9
Fe_2O_3	1.2	1	10	3
Gd_2O_3	0.7	0.8	0.7	2
K_2O	0.4	0.15	0.06	0.4
La_2O_3	0.03	0.1	0.6	0.25
MgO	0.3	<0.1	5.5	<0.2
MnO	0.1	0.35	0.05	0.9
Na_2O	0.6	0.8	0.1	2
Nd_2O_3	0.8	1	1.4	3
PbO	2.6	--	0.3	--
Sm_2O_3	0.5	0.6	0.2	1.8
SrO	0.08	0.1	0.09	0.3
ThO_2	6.2	7	19	18
UO_2	>50	65	4.5	7
V_2O_3	0.6	<0.3	2	<0.7
Y_2O_3	7.2	5	6	13
Yb_2O_3	1.5	1	1.3	3
SiO_2	12.4	4.5†	21.9	12†

*Remove from uraninite: 75% of UO_2 and 100% of PbO. Recalculate to 100%.

**Remove from uraninite: 99% of UO_2 and 100% of PbO. Recalculate to 100%.

†Using Ellsworth's value for SiO_2 in uraninite.

curve. The samples are plotted in order of decreasing uranium content. This plot affords a somewhat different perspective on the U-Th ratio as a function of uranium solution in that the effects of both uranium solution and foreign element contamination are illustrated. It can be seen that both thorium and the rare earth metals pass through a maximum at a time when the uranium solution process is virtually complete. At this point, on the average, relatively little contamination has occurred. Samples to the right of this maximum are illustrative of "contamination" of the thucholites. Uranium, thorium and rare earth concentrations decrease as iron, aluminum, magnesium and silica increase.

The suggestion that uraninite, composed almost entirely of uranium dioxide, was dissolved by naturally occurring organic materials, must be considered highly improbable. Carbonaceous materials in nature are known to reduce dissolved uranium and precipitate it as uranium dioxide, rather than the reverse. Thus one is faced with the diametrically opposing observations that (1) uranium could only be separated from the remaining constituents of uraninite by oxidation to the hexavalent (UO_2^{++}) state, and that (2) the presence of oil indicates the existence of reducing conditions.

We believe our results indicate that aqueous rather than organic solutions are responsible for the composition changes observed in conversion of uraninite to thucholite. It is true that radioactive emanations will polymerize methane to liquid and solid products, but no mechanism is available for the observed solution of uraninite. The argument that methane is present in thucholite-containing mines as a ready raw material for the formation of

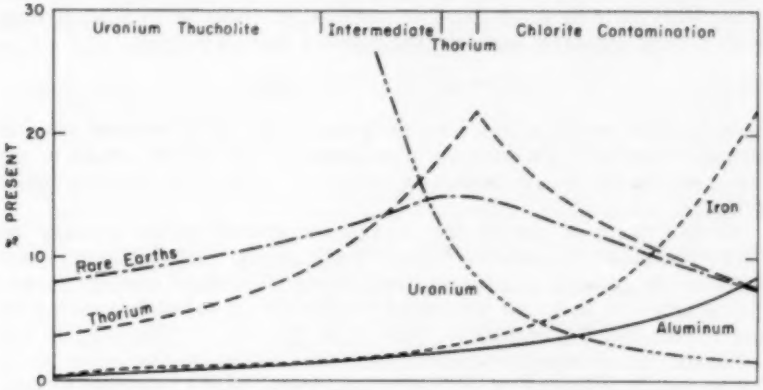

FIG. 6. Variation of ash composition of 30 Besner thucholites as a function of uranium content.

more thucholite can be answered by the experimental evidence that methane is also one of the principle decomposition products from the action of radioactivity on saturated hydrocarbons (29). It is our belief that the organic material in thucholite was carried into the pegmatite as droplets, as an oil film, or as an emulsified oil by aqueous solutions, and aided in the formation of thucholite by reduction and reprecipitation of oxidized uranium.

In our opinion radioactivity from uranium and thorium was responsible for the oxidation of uranium through its action on *aqueous* solutions coming in contact with uraninite. A simplified equation for the effects of radiation on water may be written,

$$H_2O \rightarrow \alpha H + \beta OH + \gamma H_2 + \delta H_2O_2$$

The over-all reaction may be divided into three portions termed the radical, molecular, and intermolecular reactions, but for our purposes it is sufficient to

recognize that these four products are formed, and that the average G value (number of molecules decomposed per 100 ev of radiation absorbed) of water is between 3 and 4. Types of radiation producing less ionization (γ and β rays) favor the formation of hydrogen and hydroxyl radicals, while the more densely ionizing types (α particles) result in a high yield of the molecular products, hydrogen and hydrogen peroxide. Thus a 5 Mev α particle will form approximately 10^5 molecules of hydrogen peroxide and hydrogen within a distance of 0.01 cm, its range in water [Allen (2); Dewhurst et al. (8)].

To our knowledge, the action of hydrogen and hydroxyl radicals on uranium oxides is unknown, but the action of hydrogen gas and of aqueous hydrogen peroxide has been studied. Hydrogen does not react with uranium dioxide, nor does it reduce the trioxide except at elevated temperatures (above 300° C). Hydrogen peroxide, however, is known to oxidize uranium dioxide at room temperature. Concentrations of peroxide as low as 10^{-3} molar have been shown to produce measurable oxidation in a short time. With a large excess of peroxide, the equation may be written

$$UO_2 + 2H_2O_2 \rightarrow UO_4 \cdot 2H_2O.$$

In very dilute solutions, however, the product may be a hydrated uranium trioxide, rather than the peroxide. Its comparative instability would, in any event, prevent the accumulation of a measurable quantity of uranyl peroxide in nature.

It thus becomes possible for an aqueous solution under normally reducing conditions to momentarily and locally possess oxidizing powers as a result of the passage of a radioactive particle. Oxidized uranium formed by the action of hydrogen peroxide or OH radicals is much more soluble and mobile than the tetravalent form of the element. Reprecipitation of a portion of the dissolved uranium would occur, either by the action of reducing ions in solutions, or by the organic matter that is assumed to have been associated with the aqueous solution.

It may be that many other instances of uranium migration under apparently reducing conditions can be explained by this mechanism, i.e., the uranium deposits of the Colorado Plateau, or the Witwatersrand.

We are, at present, undertaking a study of the effects of radiation on the uranium dioxide-water system. Preliminary experiments confirm the oxidation of UO_2 and uraninite by irradiation of deaerated water slurries.

Summary of Thucholite Formation

Our conclusions regarding the sequence of events in the formation of thucholite can be summarized as follows:

1. Crystallization of uraninite together with other minerals in pegmatite —approximately 800 million years ago.
2. Development of fracture zones exposing uraninite and allanite to aqueous solutions.

3. Gradual oxidation of uranium in uraninite by products of irradiated water. Solution of uranium and more soluble metal oxides. Conversion of radiating dark mineral (pyrorthite?) to chlorite. Reprecipitation of a portion of the uranium by oil carried by the aqueous solutions.

4. Oxidation and solidification of the oil together with simultaneous condensation by radiation—approximately 300 million years ago.

5. Comparatively recent re-entry of aqueous solutions carrying oil and precipating calcite, pyrite, and marcasite.

ACKNOWLEDGMENT

We are deeply indebted to Professor Clifford Frondel of Harvard University who placed the Spence collection of thucholite from the Besner Mine at our disposal. We also wish to acknowledge the valuable assistance of the analytical group of the Chemistry Division and, in particular, John Faris, who performed the many spectrographic analyses. The X-ray diffraction results were provided by Stanley Siegel and Elizabeth Gebert.

ARGONNE NATIONAL LABORATORY,
LEMONT, ILLINOIS,
April 22, 1960

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Economic Geology
Vol. 55, 1960, pp. 1739–1750

POSITION OF THE SALT-WATER BODY IN THE MAGOTHY(?) FORMATION IN THE CEDARHURST-WOODMERE AREA OF SOUTHWESTERN NASSAU COUNTY, LONG ISLAND, N. Y.[1]

N. J. LUSCZYNSKI AND W. V. SWARZENSKI

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ABSTRACT

The position and chloride concentration of a sizable body of salt water, moving slowly landward from the south-shore bays of Long Island and the Atlantic Ocean were defined by recent test drilling in the Cedarhurst-Woodmere area of southwestern Nassau County, Long Island, N. Y. Most of the salt-water body is in the lower part of a permeable artesian aquifer; the lowermost part of the salt-water body is in clay deposits underlying the permeable aquifer.

The upper limit of the salt-water body in this area was found at depths increasing progressively in a landward direction. It was 318 feet below sea level at a well in Cedarhurst and 541 feet below sea level at a well in Woodmere. The lower limit of the salt-water body was determined at depths between 578 and 630 feet below sea level in the Cedarhurst-Woodmere area. The salt-water body is more than 300 feet thick at a well in Cedarhurst, and it thins out to zero in the vicinity of a pumping center about 1¾ miles northeast of the Cedarhurst well.

Chloride concentration in the salt-water body in the Cedarhurst-Woodmere area ranged from about 40 to 16,000 ppm (parts per million). Isochlors define a zone of diffusion about a mile wide in the Cedarhurst-Woodmere area. They indicate a thickness of diffused water ranging from a few tens to more than 150 feet vertically.

Electrical-log data show that the upper boundary of the salt-water body moved upward 21 feet between 1952 and 1958 at a site in Woodmere about half a mile southwest of the pumping center. From this information it is inferred that between 1952 and 1958 the leading edge of the salt-water front moved landward about 2,000 feet toward the pumping center.

[1] Publication authorized by the Director, U. S. Geological Survey.
Prepared in cooperation with the Nassau County Department of Public Works and the New York State Water Power and Control Commission.

INTRODUCTION

An extensive salt-water body occurs in deposits of Pleistocene and Cretaceous age in southeastern Queens and southwestern Nassau Counties, Long Island, N. Y. The salt-water body extends landward into the Magothy(?) formation from surface and underground salt-water bodies in the south-shore bays of Long Island and the Atlantic Ocean.

The approximate extent of this salt-water body in southeastern Queens and southwestern Nassau Counties is described in a paper by N. M. Perlmutter and others (1). On the basis of test drilling in 1952 and appraisal of data available prior to 1958, Perlmutter and others (1, Fig. 4) estimated the leading edge of the salt-water body to be approximately half the distance of about 1¼ miles between well N3861 at Cedarhurst and well N3864 at

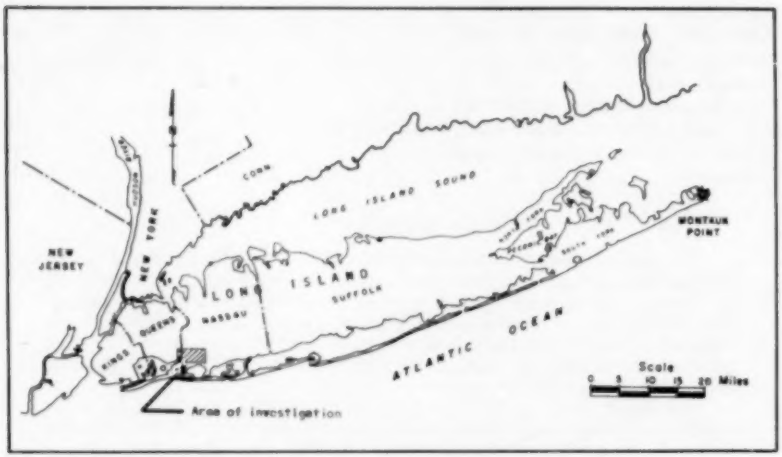

FIG. 1. Map of Long Island, N. Y., showing area of investigation.

Woodmere (Figs. 1, 2). Observation wells N3861 and N3864, drilled in 1952, are about 1¾ miles and ½ mile, respectively, southwest of a pumping station in Woodmere near Valley Stream, where ground-water withdrawals for public supply are made by a water company.

In 1958, three exploratory test holes and one observation well were drilled in Woodmere between well N3861 at Cedarhurst and well N3864 at Woodmere. The drilling in 1958 was the first phase of a program undertaken for the further investigation of salt-water encroachment in southwestern Nassau and southeastern Queens Counties, specifically for the definition of the position and the direction and rate of movement of the salt-water body. This program is being conducted by the U. S. Geological Survey in cooperation with the Nassau County Department of Public Works and the New York State Water Power and Control Commission.

Significant information on the position and chloride concentration of the salt-water body between Cedarhurst and Valley Stream at existing wells and at the test holes and well drilled in 1958 is given in this paper. Also, an estimate is made of the landward movement of the salt-water front along a section between Cedarhurst and Valley Stream. Not all the available geologic, electrical-logging, chloride-content, water-level, water-density, and pumping-test data obtained in 1958 are included in this paper. These data are to be studied together with information to be obtained in subsequent phases of the program.

The 1929 mean sea level at Sandy Hook, N. J., is the datum to which all altitudes and depths are referred in this paper. Measurements below mean

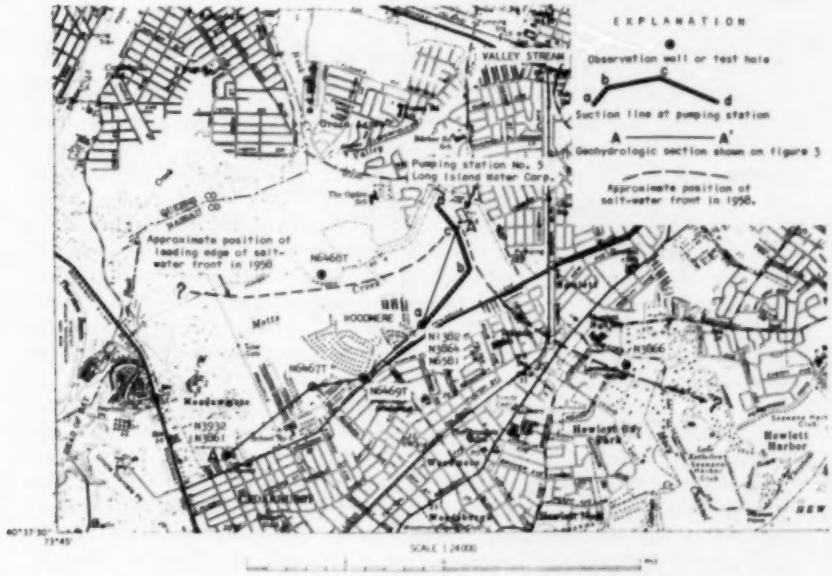

FIG. 2. Map showing the location of test holes and wells and the salt-water front in the Cedarhurst-Woodmere area.

sea level are shown by the minus (−) sign. Landsurface at test holes and wells described in this report is less than 20 feet above mean sea level.

ACKNOWLEDGMENTS AND SUPERVISION

The authors give thanks to Lee Associates and Mr. Phillip Lynne for permission to use sites on their respective properties for drilling of three exploratory test holes (N6467T-N6469T). They appreciate advice and

field supervision given by Mr. R. Sauvage, from the Research Section of the Schlumberger Well Surveying Corporation at Ridgefield, Conn., during the electrical logging of the test holes, and information furnished by the Long Island Water Corporation for well N6581. They also appreciate the support of and interest in this project of Mr. W. F. Welsch of the Nassau County Department of Public Works and Mr. A. H. Johnson of the New York State Water Power and Control Commission.

Messrs. John Isbister and Warren Teasdale of the Geological Survey assisted the authors in the collection of basic data at the exploratory test holes, in making chloride determinations, and in preliminary appraisal of the geologic information.

The paper was written under the supervision of George C. Taylor, Jr., district geologist of the Geological Survey, Mineola, N. Y.

DRILLING PROGRAM IN 1958

In 1958 the U. S. Geological Survey, the Nassau County Department of Public Works, and the New York State Water Power and Control Commission furnished funds for the drilling of three exploratory holes between existing wells N3861 and N3864 at Cedarhurst and Woodmere, respectively, and west of existing well N3866 in Hewlett Bay Park (Fig. 2). Well N3861 is about 3 miles north of the Atlantic coastline and well N3864 is 1¼ miles northeast of well N3861. The exploratory holes (N6467T, N6468T, and N6469T) were drilled during April and June 1958 by Foundation Services, Inc., of New Jersey, by the standard rotary method to depths of − 694 feet, − 699 feet, and − 698 feet, respectively. At each site, core samples were taken in a 4-inch hole, after which the hole was reamed to 6 inches for electrical logging by the Schlumberger Well Surveying Corporation.

At hole N6467T a standard Schlumberger electrical log was obtained. At hole N6468T a microlog was run in addition to the standard Schlumberger electrical log, and at hole N6469T a microlateral log was run in addition to the standard Schlumberger electrical log. Also at hole N6469T a Widco log was run to a depth of about − 555 feet by U. S. Geological Survey personnel from the Trenton, N. J., office. After the desired geologic, water-salinity, and electrical-log information was obtained, the three exploratory holes were filled with a mixture of clay and cement.

In September 1958, observation well N6581 was drilled in Woodmere by Layne-New York Co., Inc., for the Long Island Water Corporation. It was constructed near two existing observation wells, 12 feet from well N3864 and 21 feet from well N1382. The test hole for well N6581 was drilled to − 611 feet but the completed observation well was screened between − 565 and − 575 feet. Well N6581 is thus screened at the deepest level of the three wells at the site, as well N3864 is screened from − 455 to − 466 feet and well N1382 from − 167 to − 188 feet. A Widco electrical log was run by Layne-New York Co., Inc., before the hole was cased and screened. The well was test-pumped and sampled after it was completed and developed.

GEOLOGIC ENVIRONMENT

The geologic environment in the general area of southern Nassau and southeastern Queens Counties is described in detail by Perlmutter and others (1).

The geologic units in the area of the 1958 test drilling consist of a basement of Precambrian (?) crystalline bedrock sloping to the southeast, overlain by the following unconsolidated deposits in ascending order: Lloyd sand member and clay member of the Raritan formation and the Magothy(?) formation of Late Cretaceous age, Jameco gravel and Gardiners clay of Pleistocene age, and upper Pleistocene and Recent deposits. All these

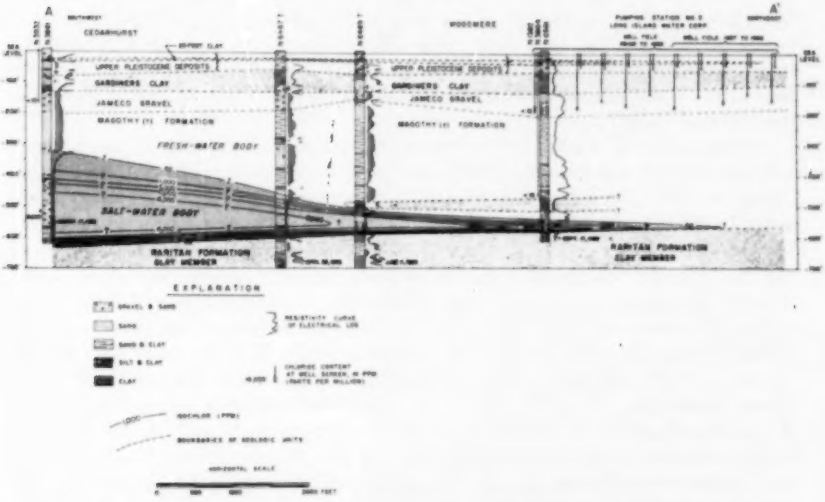

FIG. 3. Geohydrologic section A-A′ in Cedarhurst-Woodmere area of southwestern Nassau County, Long Island, N. Y.

geologic units except the Recent deposits are continuous in the Cedarhurst-Woodmere area (Fig. 3). Information obtained in 1958 and collected during the drilling of wells N3861 and N3864 in 1952 was used in part to define, more accurately than heretofore possible, the lithology and stratigraphy of the deposits from the land surface down to and including the upper part of the clay member of the Raritan formation in the area between Cedarhurst and Pumping Station No. 5 of the Long Island Water Corporation in Woodmere near Valley Stream (Figs.2, 3).

The character and lithology of the Magothy(?) formation and the underlying clay member of the Raritan formation are important to this study because the extensive salt-water body is found in these formations. The

Magothy(?) formation lies between about −150 and −600 feet in the Cedarhurst-Woodmere area. It consists of alternating layers and lenses of sand, gravel, silt, and clay, all of which appear to have limited lateral extent. The average permeability of the Magothy(?) formation at the three test holes appears to be intermediate between the rather high permeability at well N3861 and the rather low permeability at wells N3864 and N6581 (Fig. 3). At well N3861 in Cedarhurst, about 85 percent of the Magothy(?) formation consists of fine to coarse quartz sand and some gravel and a very small fraction of interstitial clay. However, at wells N3864 and N6581 in Woodmere the bulk of the Magothy(?) formation consists of very fine clayey sand and clay. The Magothy(?) at the site of wells N3864 and N6581, although containing more clay than is found commonly, corresponds closely to the Magothy(?) as it is known elsewhere in the area. The Magothy(?) deposits penetrated by test hole N6467T, which is closest to Cedarhurst, include considerable thickness of fine to coarse sand and only traces of clay. More clay content is noted in the northeasterly direction at wells N6469T, N3864, and N6581.

In general, the Magothy(?) formation contains thin lenses of solid clay, a few inches to several feet thick, but most of these apparently have short lateral extent. An exception may be a stratum of solid clay which occurs at wells N3864 and N6581 as a red and white clay in the lower part of the Magothy(?) (Fig. 3). This stratum, about 45 to 75 feet above the top of the clay member of the Raritan formation, seems to have some areal continuity. It apparently extends to the northwest and southwest for at least half a mile from wells N3864 and N6581. Its thickness is reduced in a northwesterly direction from about 40 feet at wells N3864 and N6581 to 22 feet at test hole N6468T. To the southwest, 19 feet of the material were found at test hole N6469T. However, this clay stratum was not recognized at the site of test hole N6467T southwest of test hole N6469T. The extent of this stratum in a northeasterly and easterly direction from wells N3864 and N6581 is not known, as the deepest wells at Pumping Station No. 5 are only about 200 feet deep, and as well N3866 was drilled only to −452 feet.

The top of the clay member of the Raritan formation occurs at the following depths along section A-A′ and its vicinity: −602 feet at N3861; −578 feet at N3864 and N6581; −583 feet at N6467T; −565 feet at N6468T; −580 feet at N6469T. From this information, the top of the clay member was estimated to be at about −570 feet at the pumping center of the No. 5 station, which is about half a mile northeast of well N6581.

At the test holes drilled in 1958, the upper part of the clay member consists of about 38 feet of solid light-gray and dark-gray clay, with lignite and only traces of silt. Below is a zone of more permeable fine micaceous and silty gray sand, 38 to 60 feet thick, which, in turn, is underlain by more solid and silty clay.

Test holes at the sites of wells N3861 and N6581 penetrated 14 and 33 feet, respectively, of the clay member. At well N3861, solid light- and dark-gray, brown, and purple clay with layers of lignite was found between

− 602 and − 616 feet. At well N6581 solid gray clay with thin layers of silty clay was found between − 578 and − 611 feet.

Water occurs in all the unconsolidated deposits in southwestern Nassau County. The zone of saturation extends to and into bedrock from depths of about 1 to 10 feet below the land surface. The land surface in the Cedarhurst-Woodmere area is in general less than 20 feet above mean sea level.

Water in the Magothy(?) formation and the Jameco gravel is confined between the Gardiners clay above and the clay member of the Raritan formation below. Water above the 20-foot clay unit in the upper Pleistocene deposits is unconfined; that below the 20-foot clay is confined, as the 20-foot clay is apparently continuous in the Cedarhurst-Woodmere area.

CHLORIDE CONCENTRATION AT TEST HOLES

Chloride concentration of water at the test holes was determined principally by analysis of the natural water content in core samples obtained during the test drilling. Most of the core samples were taken with a split-spoon core barrel 1½ inches in diameter and 18 inches long. A few samples 3 inches in diameter and as much as 5 feet long were obtained by a rotating double-walled coring device.

Fluorescein dye (400 ppm) added to the drilling fluid colored it green and identified core samples invaded by the drilling fluid. The formational water from uninvaded cores was analyzed for chloride content by two methods developed during drilling test holes N6467T-N6469T. These methods are described in detail by Swarzenski (2). A brief résumé of the methods is given below.

The first method, involving centrifugal extraction, is comparatively simple and apparently yields reliable results, if cores are obtained and preserved properly at the time of the drilling. The second method, termed the "dilution method," was devised for fine-textured samples—solid and silty clays, which did not yield sufficient water by centrifugal extraction. The laboratory procedure for the dilution method requires a determination of moisture content from the loss in weight of a core when it is dried in an oven, the restitution of original moisture content and further dilution with distilled water, resolution of the salts precipitated during drying, and filtration.

This technique must be considered experimental because of several unknown factors. However, results of the correct order of magnitude were obtained in the laboratory. Thus, the use of the dilution method seems justified, at least as a semiquantitative tool, in the determination of brackish and saline ground-water zones. In general, chloride values determined by the dilution method were in agreement with chloride concentrations determined by the centrifuge-extraction method and with known ground-water salinities in the area. It is considered that reasonably accurate data are obtained by the dilution method for formational water having a chloride concentration in excess of 200 parts per million.

Chloride concentrations determined by the centrifuge-extraction and/or

TABLE 1

CHLORIDE DETERMINATIONS OF WATER FROM CORE SAMPLES OBTAINED IN 1952 AND 1958

a—Depth, in feet below sea level.
b—Chloride content, in parts per million, by centrifuge-extraction method.
c—Chloride content, in parts per million, by dilution method.
d—Order of magnitude defined (see note below).

N3861		N3864		N6467T			N6468T			N6469T		
a	c	a	c	a	b	c	a	b	c	a	b	c
—	—	560	d_{10}	—	—	—	—	—	—	—	—	—
596	$d_{3,700}$	569	$d_{1,000}$	38	62	—	15	500	—	473	<20	—
605	$d_{4,200}$	579	d_{700}	457	<25	—	35	6,600	—	505	—	<50
615	$d_{1,900}$	—	—	477	1,300	—	55	7,500	—	511	<60	—
—	—	—	—	496	7,700	—	76	—	<10	527	>4,600	—
—	—	—	—	516	12,500	—	95	—	<20	536	12,700	—
—	—	—	—	537	16,000	—	95	Fresh water		560	10,800	10,200
—	—	—	—	576	—	10,800	699	(<40)		565	10,500	—
—	—	—	—	597	—	1,400	—	—	—	570	10,700	—
—	—	—	—	616	—	<15	—	—	—	573	—	8,700
—	—	—	—	—	—	—	—	—	—	575	—	7,900
—	—	—	—	—	—	—	—	—	—	580	—	1,020
—	—	—	—	—	—	—	—	—	—	597	—	<50

Note: Cores for wells N3861 and N3864 taken in 1952 and chloride determinations made in 1958. Original water content estimated, as cores had dried out. Determinations of chloride content approximate.

Chloride determinations at time cores were obtained: in April 1958 at test hole N6467T, in May 1958 at test hole N6468T, and in June 1958 at test hole N6469T.

dilution methods for test holes N6467T, N6768T, and N6469T are listed in Table 1.

SALT-WATER BODY IN THE CEDARHURST-WOODMERE AREA

In the Cedarhurst-Woodmere area, fresh water in the Magothy(?) and deeper formations under natural conditions has generally much less than 20 ppm of chloride content. Chloride concentrations in excess of 20 ppm in these formations thus indicate the presence of an additional source of chloride. The only known additional source of chloride, natural or otherwise, in the Magothy(?) and deeper formations in the Cedarhurst-Woodmere area is sea water. Chloride concentrations in excess of 20 ppm are then the first indications, and those in excess of 40 ppm are positive indications, of the mixing of fresh water with sea water. For this report, a "salt-water body" is defined as one having mixtures of fresh water and sea water, the chloride concentration in the salt-water body ranging between 20 to 40 ppm and 16,000 to 18,000 ppm. A salt-water body so defined includes the salty or diffused water between fresh water and sea water.

The position and chloride concentration of the salt-water body in the Magothy(?) formation and the clay member of the Raritan along section A-A' (Fig. 3) between well N3861 in Cedarhurst and the pumping center in Woodmere were defined by (1) the resistivity curves of electrical logs for

test holes and observation wells, (2) the chloride concentrations determined by the centrifuge-extraction and/or dilution methods, and (3) the chloride content of water sampled at observation wells. For this purpose, data obtained at wells N3861 and N3864 drilled in 1952 and at test holes N6467T-N6469T and well N6581 drilled in 1958 were used. In general the resistivity curves of electrical logs defined adequately the upper and lower limits of the salt-water body. The chloride concentrations in the salt-water body were determined principally by the centrifuge-extraction method, by the dilution method, and from water samples at finished wells.

The electrical log and the chloride concentrations determined by the dilution method at well N3861 show the salt-water body as lying between about − 318 and − 630 feet. The upper limit of the salt-water body was determined from the electrical log. The lower limit was based on the chloride concentration of approximately 1,900 ppm indicated in 1958 by an analysis made from a core sample taken at − 615 feet in 1952 (Table 1). The core had dried out between 1952 and 1958, and thus it was necessary to estimate the original water content in the sample. However, the determination suggests at least the proper order of magnitude of the chloride content, and the evidence is sufficient to show salt water at − 615 feet. From this, it is estimated that the lower limit of the salt-water body at the site of well N3861 is about 15 feet deeper than the bottom (− 615 feet) of the hole, or at about − 630 feet.

Water at the screen (− 515 to − 526 feet) of well N3861 had a chloride concentration of about 16,000 ppm between 1952 and 1958. In water at the screen (− 165 to − 169 feet) of observation well N3932, located at the site of well N3861, chloride concentrations of less than 10 ppm were observed between 1952 and 1958.

Electrical logs and chloride determinations by the centrifuge-extraction and dilution methods show the salt-water body to be between − 464 and − 600 feet in April 1958 at test hole N6467T, and between − 511 and − 583 feet in May 1958 at test hole N6469T. The observed maximum chloride concentration in the salt-water zone, as determined by the centrifuge-extraction method, was 16,000 ppm at test hole N6467T and 12,700 ppm at test hole N6469T. That at test hole N6469T may not be the maximum in the salt-water zone.

An electrical log run in September 1958 in well N6581 in Woodmere indicated a salt-water zone between − 541 and − 582 feet at and near the bottom of the Magothy(?) formation. Water at the well screen (− 565 to − 575 feet) had a chloride concentration of about 8,000 ppm in October 1958. The screen was set at a depth where the resistivity curve of the electrical log suggested the highest chloride concentration. Water at wells N3864 and N1382 had a chloride concentration of less than 10 ppm. These two wells, located at the site of well N6581, are screened from − 455 to − 466 feet and from − 167 to − 188 feet, respectively.

Available data indicate that the upper limit of the salt-water body is in the Magothy(?) formation, and that it is beneath the red and white clay between test hole N6469T and well N6581, as shown in section A-A′. The

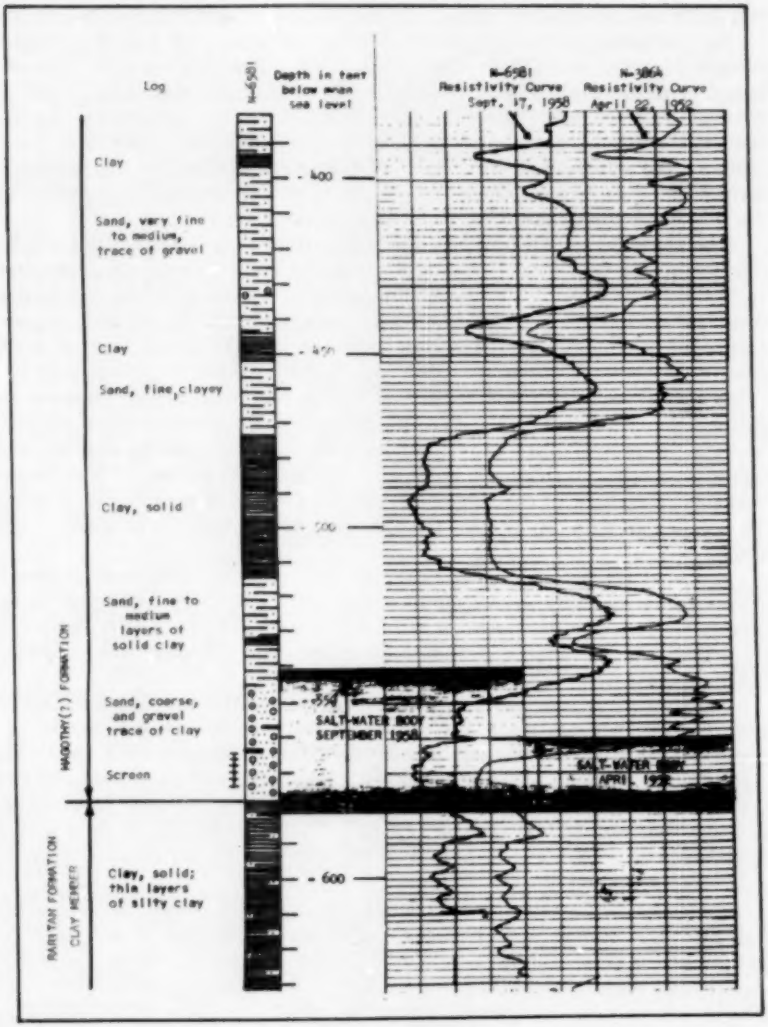

FIG. 4. Thickness of the salt-water body in April 1952 and September 1958 at site of wells N3864 and N6581 in Woodmere.

lower limit of the salt-water body penetrates the uppermost part of the underlying clay member of the Raritan formation, which contains salty water to a depth of about 28 feet below the top at well N3861, about 17 feet at test hole N6467T, about 3 feet at test hole N6469T, and about 4 feet at

well N6581 below the top of the clay member. The lowermost part of the salt-water body is believed to be in nearly solid clay along section A-A′

The isochlors shown in section A-A′ (Fig. 3) are best defined at test holes N6467T and N6469T, where determinations of chloride content were made by the centrifuge-extraction and the dilution methods. Those at well N3861 and at wells N3864 and N6581 are based on the resistivity curve, chloride concentrations at the well screen, and determinations in 1958 by the dilution method from cores taken in 1952 near the bottom 20 feet of the hole (Table 1).

The chloride concentrations in the salt-water body along section A-A′ are at a maximum as much as 50 feet, and perhaps more, above the top of the clay member. They decrease landward from about 16,000 ppm at well N3861 and N6469T to about 8,000 ppm at well N6581 and to less than 40 ppm near the pumping center. Along the top of the clay member, the chloride decreases from about 12,000 ppm at well N3861 to about 8,000 ppm at test hole N6467T to about 1,000 ppm at test hole N6469T, and to probably less than 1,000 ppm at well N6581 (Fig. 3). The zone of diffusion is at least a mile wide along section A-A′. The thickness of the zone of diffusion in a vertical direction ranges from a few tens of feet to more than 150 feet along this section.

In 1958 the salt-water body was observed to decrease in thickness from more than 300 feet at well N3861 to 72 feet at test hole N6469T and 41 feet at well N6581. The salt-water wedge apparently thins out to zero at or near the pumping center about half a mile landward from well N6581. Available information does not allow pinpointing the position of the leading edge of the salt-water front. However, apparently the leading edge is within at least a quarter mile of the pumping center at the No. 5 Pumping Station.

The leading edge of the salt-water front is at the bottom of the Magothy(?) formation and at or near the top of the clay member. It is apparently about 400 feet below the bottoms of the deeper supply wells screened in the Jameco gravel at the No. 5 Pumping Station. Thus, fresh-water supplies at the station are in little immediate danger under present (1959) conditions. A plan view of the estimated position in 1958 of the leading edge of the salt-water front in the vicinity of section A-A′ is shown in Figure 2. The position is based in part on conditions shown in Figure 3, and on finding no salt water in the Magothy(?) formation and in the clay member at test hole N6468T drilled in 1958. It is also based on indirect evidence which suggests that the leading edge of the salt-water front may be in the vicinity of or at well N3866 at depths of about 200 feet below the screened zone at − 395 to − 405 feet at and above which only fresh water was found.

MOVEMENT OF THE SALT-WATER FRONT

The resistivity curve of the electrical log at well N6581 and the chloride content of the water sampled at the screen (− 565 to − 575 feet) of well N6581 defined the presence in October 1958 of a diffused-water zone 41 feet thick between − 541 and − 582 feet at and below the bottom of the Mag-

othy(?) formation. The presence of salt water in this zone at this site was first suggested by chloride determinations (Table 1) made in 1958 by means of the dilution method on cores taken in 1952 at well N3864. Wells N3864 and N6581 are about 12 feet apart at the same site. The presence of salt water was confirmed subsequently by the chloride content of 8,000 ppm in October 1958 in water at the screen of well N6581. Thus it was possible to interpret with assurance the resistivity curve of the electrical log for well N3864 as demonstrating a salt-water zone 20 feet thick between about − 562 and − 582 feet in April 1952.

As indicated by the side-by-side comparison of the resistivity curves for wells N3864 and N6581 given in Figure 4, the salt-water body thickened at the site of well N6581 between April 1952 and October 1958. The thickening produced an upward movement of about 21 feet in the upper limit of the salt-water body. The upward movement in all likelihood was accompanied by a landward advance of the leading edge of the salt-water front toward the pumping center. The landward advance is estimated to be on the order of 2,000 feet on the basis of the slope of the upper boundary of the salt-water front. The slope at well N6581 was approximately 20 feet in 2,000 feet (1%).

The upward and landward advance of the salt-water front was caused by the effects of continuous pumping from wells at the Mill Road Station near Valley Stream. Withdrawals at the Mill Road Station averaged about 7 mgd (million gallons per day) between 1945 and 1952 and about 5 mgd between 1953 and 1958. They were made from as many as 150 wells screened in the upper Pleistocene deposits and in the Jameco gravel along the common suction line at the No. 5 Station. Originally the dogleg suction line consisted of sections *ab*, *bc*, and *cd* (Fig. 2) and was 3,900 feet long. Its southeast end was at well N1382. However, in July 1957 section *ab* (1,900 feet long) was abandoned, and since then about 100 wells are pumped along sections *bc* and *cd*.

More than half the total withdrawal is made from the Jameco gravel, but the exact amount is not known. Nevertheless, the withdrawals create a sizable cone of depression in the piezometric surface not only in the Jameco gravel but also in the full thickness of the Magothy(?) formation. To the southwest the cone of depression extends beyond wells N3861 and N3932 at Cedarhurst. Thus the salt-water body between Cedarhurst and the pumping center also is within the cone of depression.

U. S. Geological Survey,
Mineola, New York,
April 4, 1960

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Economic Geology
Vol. 55, 1960, pp. 1751–1756

COMMENTS REGARDING THE BLIND RIVER (ALGOMA) URANIUM ORES AND THEIR ORIGIN

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ABSTRACT

More is daily becoming known about the nature of the Algoma (Blind River) uranium deposits and, accordingly, opinions on their origin may now be more meaningful.

In the first published description of the field (7) following its discovery in 1952 I then omitted reference to the possible origin of the ores but tacitly implied that they were probably hydrothermal and hypogene by identifying the field as centrally situated in a large metallogenetic province characterized by the classical hypogene mineral assemblage of cobalt-nickel-uranium. I am now having second thoughts on the subject. Observations on new data and my opinions follow. The presently suggested theory does not mark the end of the road but rather another milestone.

ROCKS AND STRUCTURE

First, a brief review of the structure and rock types of the Algoma field in order to correct several earlier misconceptions. The present synclinal trough form of the Algoma (Blind River) uranium area is not a sedimentary primary structure, but a secondary one; it is the product of subsidence, folding and to a lesser degree faulting, of an original uniform slope dipping southerly at gentle angles over the entire region. This is now clearly evident from the uniform southwardly thickening of all beds of the ore-bearing Mississagi series and by detail of internal structure such as cross-bedding, pebble size variation and alignment (13). Statistical studies indicate an origin for the basal conglomerate materials "130 to 250 miles W.N.W. of Thessalon" (3) or 160 to 280 miles westerly from Blind River.

These facts now refute the earlier assumption by Collins (1), myself, and followers that the important North and Middle Belts of the north portion of the field were the flanks of a sedimentary syncline (the "Basin").

The "South Belt" (principally Pronto Mine) is probably also a segment of this same uniform, originally south-dipping sedimentary slope now steeply inclined, folded and much faulted by the Murray Fault system of regional importance.

The geological sequence in the Algoma area now appears to have been sedimentary deposition of products from the Archean "basement" terrain of the northwest, throughout the Mississagi period; folding, in (large?) part due to vertical settling as indicated by the sedimentary basin attitude of younger overlying sediments, climaxed by regional thrust faulting with gentle dips southerly, and offsets up to one-quarter mile accompanied by more numerous steep-dipping normal faults.

Some intrusion and replacement by material of gabbroic composition, principally into the "basement" rocks, took place; most of it prior to faulting activity. The gabbroic material is associated with minor quantities of an albite-rich material becoming more important, volumetrically, at a slightly later period. The gabbroic material is locally rich in iron sulfides. At the Pronto mine and reportedly at other points in the "Basin" area, the gabbroic material appears originally to have been present as sill-like masses in the top of the Archean rocks roughly conformable to and underlying the ore-bearing conglomerates, basal to the overlying Mississagi sediments. Where shafts and crosscuts have cut the basement rocks some exposures reveal that much of the gabbroic material has been involved in faulting at the base of the sediments and now locally presents the aspect of a basic matrix to brecciated "basement" rock fragments.

Most of the albite-rich facies came somewhat later, and was less pervasive and more incisive in its mode of implacement. Its distribution has been recognized at several points underlying the uranium-bearing areas. In most places it is known only to cut the "basement" rocks but at the Pronto Mine it cuts and replaces the uranium-bearing conglomerate, changing completely its petrographic and mineralogic nature (but without seriously affecting its uranium content!).

Late in the above sequence, several large dikes and sills of diabase appeared. These are seemingly later than much of the faulting. They apparently avoided the compressive thrust faults in preference to more "open" normal faults and tension fissures.

MINERALIZATION

In regard to the mineralization of the ore-bearing conglomerates, it is now reasonably certain that the uranium minerals and the pyrite (with lesser pyrrhotite) were present prior to the folding, faulting, and cataclastic fracturing of the ore-bearing rocks. All faults that cut or displace the sulfide and uranium-bearing conglomerates, both regional and subsidiary, have been found to be unmineralized and show no evidence of hydrothermal activity. The commonly fractured quartz pebbles of the conglomerate are unmineralized except for rare smears of marcasite-like paint obviously derived from the quite plentiful (3 to 10%) source of granular pyrite confined to the conglomerate matrix. It is also evident that the uranium minerals and iron sulfides pre-date the diabase dikes and sills that cut and displace the ore beds, in places affecting the mineralogy (by conversion of iron sulfides to oxides and seemingly the earlier uranium minerals to pitchblende. The latter, in places with a pink calcite gangue, is then found as fracture fillings in the conglomerate, the quartzite, or near the edges of the diabase).

The uranium minerals and iron sulfides are clearly earlier than the albite-rich intrusives that underlie and intrude the Pronto Mine (less well-known masses of albite granite also underlie the north rim of the "Basin"). At the Pronto Mine the normally white to gray albite-rich rock has, to a varying degree, replaced the conglomerate ore bed, changing it into a red-colored,

crystalline, albite-rich mass with a few quartz "eyes" (undigested remnants of quartz pebbles). This interesting phenomenon has converted the iron sulfides to oxides and the earlier implaced uranium minerals to secondary types. The resulting "pink" albite-rich ore layer conforms perfectly in position to the original conglomerate ore-bed and has about the same thickness. The mining of several thousand tons of this material has indicated a uranium content only slightly below that of the original conglomerate into which it transitionally changes "on strike." Some vugs measuring several inches across occur in this unusual material and are in places lined with pink colored calcite or massive lumps of chalcopyrite. Magnesite is also locally conspicuous in this altered ore.

In detail a study of the Algoma mineralization is perplexing. It has very few characteristics that one commonly attributes to either beach or river placer deposits, with both of which types I have had some personal experience. There are in reality few of the customary placer detrital "heavy minerals" present despite still constant claims to the contrary (12); iron is plentiful but almost entirely as fresh sulfides. There is no recognizable specific gravity stratification of the minerals, other than a random distribution in the conglomerate beds; no specific concentration towards the base (original "bed-rock") of the conglomerate bed or upon quartzite inter-layers that might have served as false "bed-rock" shelves within the conglomerate horizon, as would be the case with distribution of detrital minerals by river placer; nor are the minerals consistently concentrated towards the top of interbeds, as might be more naturally expected with beach (surf-wind) placers. The iron sulfides have a quite general distribution throughout the conglomerate beds and to a lesser degree graywacke "grits" of the same stratigraphic horizon, with a suggestion of random streakiness generally conformable to the bed, or locally to cross-bedding within it.

The distribution pattern of the radioactive minerals show a good general correspondence with that of the iron sulfides, although there appears to be no very direct quantitative relationship.

The iron sulfides (principally pyrite) occur entirely as discrete individual grains, commonly as fractured crystals containing minute specks of sericite. There is no evidence of fracture filling by sulfides or uranium minerals although the rare fractured face of a conglomerate quartz pebble has been smeared by friction products of iron sulfide. Accretion clusters of many minute grains of iron sulfides are occasionally seen in the ore-bearing material. In attempting to visualize the mechanics of entry and emplacement of the iron sulfides, from viewing many ore sections, I conclude that they originated as disintegration products of pyrite-bearing rocks (from the Archean basement), were transported in a medium of high density silt-laden water that inhibited oxidation and inhibited effective gravitation settling or stratification.

The Algoma pyrite may well have been derived from large pyrite masses similar in type to those described (5) as occurring in the extensive Archean "basement" terrain in the region to the immediate north of the uranium area, and classified as "of submarine exhalative sedimentary ore body type".

Some preliminary pyrite thermometry tests have been performed on

pyrite specimens from the ore beds taken at several points in the Algoma field. The test results are not clear-cut but, in general, the decrepitation temperatures fall into two groups, one ± 650° C, the other, and much smaller group ± 350° C. Some of the material producing the lower temperature result is identifiable as smear material on fracture faces of crushed quartz pebbles. The higher temperature results are described as typical for material "of pegmatitic origin or derived from highly metamorphosed terrain" (14).

The most common and most important uranium minerals present are uraninite and brannerite. Patchett, (11) who has recently made an intensive study of three ore specimens from the Algom Nordic mine, states that uraninite is much more plentiful than brannerite; the uraninite occurs as uniform, small (0·1 mm) euhedral cubic crystals showing a zoned development with the purest composition outermost and surrounding a core of impure material mixed with a probable hydro-carbon. The uraninite is confined to a sericite matrix. The uraninite occurs as single crystals or as accretion clusters of numerous minute grains.

The brannerite occurs as an intimate mixture with quartz. Such mixed grains occur as small prismatic crystals with apex oriented towards the centre. The perimeter is purest. A common impurity of the brannerite is anatase occurring in varying amounts. No apparent hydrocarbon occurs with the brannerite.

Patchett (11) also recognized very small amounts of pitchblende and coffinite occurring as the probable modification products of other and earlier uranium minerals.

The distribution of the uranium minerals has been described as roughly similar in pattern and place to that of the iron sulfides. They show few, if any, of the characteristic features of detrital origin and a similar lack of evidence of hypogene origin.

There is one feature about the occurrence of the uranium in the Algoma field that is noteworthy. It is the uniform content of uranium in the conglomerate. Over several square miles in area, averaging about ten feet in thickness and totalling several hundred million tons, the uranium-bearing material averages about 0.12% U_3O_8 with amazing consistency and despite considerable variation in detail. I feel that this feature suggests the delicate yet extensive chemical control of solubility and precipitation that could only have been exercised by a large volume (area) of uranium-laden solution, soaking the permeable silt pebble horizon at one time.

In view of the universally recognized solubility of practically all uranium minerals at low temperatures (2), the mineralogical characteristics of the uraninite and brannerite present, the absence of detrital evidence and the absence of evidence commonly diagnostic of hypogene hydrothermal origin, I suggest that the uranium mineralization of the Algoma field is syngenetic and was introduced by ground water solutions that had leached and concentrated its uranium content from probably low-grade Archean "basement" areas. It is possible that the uranium-bearing waters were the same that transported the pyrite-bearing silt and gravel mixture of the resultant con-

glomerates. This view is a variation of the placer or detrital origin, first proposed by Holmes (6) and Robertson (12) who visualize the physical transport of the material, but is believed similar in part to the origin proposed by Derry (3) without accepting Derry's reliance on "the agency of organic material."

The theory of origin suggested and which I consider the most tenable for the Algoma uranium minerals, may have much wider application. It appears more than a coincidence that basal sediments of any age, but immediately overlying the Archean "basement," are quite commonly uranium-bearing. The Witwatersrand, Algoma (Blind River), Beaverlodge, Brazil's Jacobina Mine, Rum Jungle, and lesser known fields such as Vastervik in Sweden, are examples of the case where the overlying sediments are of Proterozoic age; the several uranium-bearing "Kolm" fields of Sweden and northern Europe illustrate the case where the overlying sediments are of Cambrian or early Paleozoic age; the Buller's George field of New Zealand and Uravan and Grand Junction fields of the "Colorado plateau" are examples of the case where the overlying sediments are of Mesozoic age. This general observation is another way of expressing (and explaining?) an earlier observation by Lang (8) that most important uranium-bearing fields appear to occur at or near the peripheries of Precambrian shield areas. Could such a stratigraphic position not indicate a relationship between source material and resultant syngenetic sedimentary origin; not as detrital deposits, which appear improbable in view of the solubilites involved, but as chemical solution deposits?

The Algoma uranium field is fringed to west and north and less so to the east, by many small pitchblende deposits that serve to define an extensive uranium metallogenetic province. All these fringe deposits are strikingly similar. Some comment concerning them is called for in any discussion of the origin of the Algoma conglomerate deposits. They consist of narrow, lensy fracture fillings of pitchblende and pink colored calcite, filling tension cracks within or occurring along the contacts of dikes or sills of basic composition (locally called "diabase" or "gabbro"). In places a little cobaltiferrous chalcopyrite is also present. The only expressed view as to the origin of this type of uranium deposit is by Nuffield (10). He states "The genetic relation between diabase and pitchblende in this area deserves serious consideration." I believe that such deposits are indeed genetically related to their basic host, at least in the sense described by Emmons, Reynolds and Saunders (4), that the basic dike material (their lamprophyre) acted as a collector and sponged the uranium from the rock it cut which is, in every case of the deposits described, the Archean basement or the same source rock regarded as the supplier for the conglomerate type uranium ore.

TORONTO, CANADA,
July 14, 1960

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Economic Geology
Vol. 55, 1960, p. 1757

SCIENTIFIC COMMUNICATIONS

GOLD AND SILVER IN MANGANESE ORE, POLK CO., ARKANSAS

LYNDON L. FOLEY

Manganese deposits, occurring in the massive upper and lower members of the Arkansas Novaculite, are considered by Miser (1) to have been leached from the country rock and deposited in fractured zones in the novaculite.

Some of the manganese deposits contain copper and some contain phosphorous, commonly above the tolerated limit of 0.25% which requires mixing the ores of different localities. Mr. Will Hargus (2), manganese buyer at Mena, Arkansas, reported an occurrence at Short Creek south of Shady, Arkansas, which averaged 1.4% copper and was kind enough to furnish a sample from Pit No. 5. It was soft, sooty manganese ore with no trace of copper visible to the eye. An assay by Charles O. Parker of Denver showed copper 1.4%, gold 0.02 oz. per ton and silver 0.67 oz. per ton.

Non-commercial traces of gold and silver have been reported in many localities in the Ouachita Mountains of Arkansas. Emmons (3) reported that gold may be dissolved in the presence of manganese if there are any chlorides in the water. It is suggested that the gold and silver may have been leached from the country rock and transported with the manganese.

TULSA, OKLAHOMA,
June 27, 1960

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Economic Geology
Vol. 55, 1960, pp. 1758–1759

DISCUSSION

ILMENITE, MAGNETITE, AND FELDSPAR ALTERATION UNDER REDUCING CONDITIONS

Sir: The "Discussion" by Dorothy Carroll in this Journal (3) confirms my own conclusions regarding a favorable environment for alteration of ilmenite to titania. Dr. Gruner (4) altered ilmenite to rutile and pyrite at elevated temperatures in the presence of H_2S. Langtry Lynd (6) found sulfuric acid and humic acids most effective, and alkaline solutions ineffective, in altering ilmenite at room temperature. Alteration products were rutile and iron oxide.

In a study of alteration of the Jurassic upper Morrison host rocks of uranium deposits in McKinley and Valencia Counties, New Mexico (2), I found evidence that authigenic kaolinite, pyrite, and anatase superseded and partially replaced detrital feldspar and vanished detrital magnetite and ilmenite, and probably were all formed during a single period of postdepositional alteration. Thus an acid reducing environment was postulated, in which alteration was accomplished by fluids containing possible combinations of humic and sulfuric acids, H_2S, and other compounds and complexes of sulfur.

In these sandstones, I found only garnet, tourmaline, zircon, micas, chlorite, and leucoxene (probably rutile and/or anatase) among the detrital heavy mineral suite. Gruner and Knox (5) report apatite and rutile in addition. Although no magnetite, ilmenite, titanite, amphiboles, or pyroxenes were found, it is logical to infer the former presence of at least some of these species as normal constituents of an immature arkosic sediment. The virtual disappearance of many feldspar grains, especially of sanidine, leaving shells similar to those described by Miller (7), was quite evident; and hollow, geodelike partial pseudomorphs of anatase, and a little pyrite, after detrital grains, were interpreted as replacement or supersedure of iron- and titanium-bearing minerals.

As Carroll suggests, much of the iron to form pyrite probably comes from minerals other than ilmenite. Iron could also be derived from magnetite; and TiO_2, to form rutile, anatase or brookite could come from other titanium-bearing minerals as well as ilmenite. Considering her speculations regarding the effect of reducing conditions on the alteration of garnet, it is interesting to note that I found apparently unaltered fragments and euhedral crystals of pink to light brownish red garnet in the Morrison sandstones, although a few garnets were somewhat etched and some varieties may have disappeared entirely.

In a letter dated October 9, 1959 to Mr. Lynd, concerning the alteration of ilmenite now found in beach sands of New Jersey, I postulated conditions very similar to those outlined by Carroll:

> It seems likely to me that most ilmenite grains come to rest many times before they reach the beach deposits. Some of them may remain for long periods of time buried in sediments, perhaps at shallow depth, but below the zone of oxidation. Many may remain indefinitely in swamps, under bayous or lagoons, in sediments rich in organic matter, or in other similar environments where the concentration of humic acids and sulfur would be many times that in rain water.
>
> Thus, I believe that the major part of the alteration of the sand ilmenites took place neither in the crystalline rocks nor on the beach, but while they were buried in sediments during their journey. The great variation in amount of alteration of individual grains would be due in part to differences in duration or other conditions of burial.

As a matter of fact, some of the beach ilmenite of New Jersey may have spent considerable time in Cretaceous sediments similar to those described by Carroll but tributary to the New Jersey beaches. However, except for the time factor, burial under similar reducing conditions in Tertiary, Pleistocene, or even transient Recent sediments should produce similar alteration.

Although van Andel (1) has assigned a minor role to post-depositional alteration (intrastratal solution), it appears that post-depositional processes involving reducing conditions are fully as effective as weathering in altering ilmenite and perhaps magnetite and other iron- and titanium-bearing minerals, and perhaps even some varieties of feldspar. Thus the maturity of a sediment as indexed by the disappearance of these and perhaps other minerals may reflect not only exposure to weathering and distance from source but also the duration and intensity of alteration under reducing conditions during burial.

S. RALPH AUSTIN

U. S. ATOMIC ENERGY COMMISSION,
GRAND JUNCTION, COLORADO,
Sept. 27, 1960

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Economic Geology
Vol. 55, 1960, pp. 1760–1775

REVIEWS

SHORT REVIEWS OF NEW RUSSIAN BOOKS

Kratkii kurs geologii SSSR. [Brief course on the geology of the U.S.S.R.] By E. D. Shlygin. Pp. 271; figs. 46. Gosgeoltekhizdat, Moscow, 1959. Price, 10r. 85k.

This course on the geological structure of the Soviet Union has been written for use in technical schools and universities. It is crammed with information on regional stratigraphy, and it is accompanied by a useful colored sketch-map (1:25 m) depicting the main tectonic elements of the country in a simple way. In its compilation of detail, however, the book approximates more to a reference work than a teaching text and so becomes somewhat dull reading. Much of it seems to be based on the well-written sketch of the geology of the U.S.S.R. by Professor Nalivkin, and on the short book on tectonics by the late Professor Shatsky, both of which are now available in English, French, and German translations. There is no mention at all of the contemporary three-volume compilation on "The Geological Structure of the U.S.S.R." edited by Markovsky, which forms the most up-to-date and comprehensive source-book on Russian geology. (A French translation of this last work is in course of publication by *Centre National de la Recherche Scientifique*, with seven fascicules issued to date.) Unfortunately none of these publications is sufficiently elementary for use in a course to Western undergraduates. For this purpose the excellent geological articles with colored and other maps in the U.S.S.R. volume of the Great Soviet Encyclopaedia (vol. 50, 1957) merit publication in English translation.

Regional'naya stratigrafiya Kitaya. [Regional stratigraphy of China.] Pp. 660, 4to. Inostranizdat, Moscow, 1960. Price, 46r.

Since J. S. Lee published his "Stratigraphy of China" (London, 1939), no major text on Chinese geology has appeared other than in ideographs, and modern advances in knowledge are largely unknown in the West. A special interest therefore attaches to this Russian translation of an extensive work by some 25 Chinese authors, the original of which was published in 1956 by the Academy of Sciences of the Chinese Nationalist Republic. In a key sketch-map the whole territory of China is divided into 119 natural regions. Details of the stratigraphy of all these districts were not available for publication, but stratigraphical tables with descriptions of the individual formations are presented for 81 such provinces. The country left undescribed includes the districts of strategic importance such as Tibet, the borderland of Burma and Indo-China, and all the coastal belt south of Nanking, as well as regions where there is no solid geology such as the basins of the lower Hwang Ho and lower Yangtze Kiang. Problems of transcription and transliteration may be overcome by the use of a Russian atlas of China. There are indexes

of geological formations and geographical names, and a bibliography of around 2,000 items is arranged on a regional basis.

Zakonomernosti razmeshcheniya poleznykh iskopaemykh. [Regularities in the disposition of ore deposits.] Vol. II. Pp. 504. Academy of Sciences, Moscow, 1959. Price, 37r.

The second large volume of articles concerned with establishing the causal relationships between metallogenesis on the one hand and magmatism or tectonics on the other follows the same lines as the first (ECON. GEOL., v. 54, p. 1325). There are 24 contributions. Those of more general interest include articles on the regional metallization of Europe (Zakharov), on a metallogenetic map of the U.S.S.R. for iron (Sokolov), on the genesis and classification of copper ores (Domarev) and uranium ores (Semenov), and on the relationship of placer deposits to climatic conditions (Trofimov). Most of the book is taken up accounts of various ore provinces in the U.S.S.R. A good many of the conclusions seem somewhat platitudinous. Colored plates depict the mineral provinces of Europe and the iron ore fields of the Soviet Union.

Povedenie zolota v zone okisleniya zoloto-sulfidnykh mestorozhdenii. [The behaviour of gold in the zone of oxidation of auriferous sulphide deposits.] By V. M. KREITER, V. V. ARISTOV, I. S. VOLYNSKII, A. N. KRESTOVNIKOV and V. V. KUVICHINSKII. Pp. 268; figs. 103. Gosgeoltekhizdat, Moscow, 1958. Price, 13r. 90k.

This well documented and clearly written monograph deals with observations on the distribution of gold in the primary and principally in the supergene zones of the sulphide ore deposits in the Maikain ore field (85 pp.) and of Dzhusaly (50 pp.) in Kazakhstan, and of Blyava and Novyi Sibai in the southern Urals (18 pp.). There are chapters on current ideas about hypogene and supergene gold, on the formation of secondary auriferous zones, on experimental and theoretical work concerning the solubility of gold, on conditions for the solution and migration of gold in the zone of oxidation, and on practical problems arising in the mineragraphic study of gold ores. On a cursory review one gains the impression that the work is an outstanding contribution to a much-debated topic.

Geologiya v Rossii pervoi poloviny 19 veka. [Geology of Russia in the first half of the 19th century.] By V. V. TIKHOLMIROV. Pp. 228, 2 maps. Academy of Sciences, Moscow, 1960. Price, 11r. 70k.

The Geological Institute of the Academy of Sciences established a special division for the study of the history of geology in 1956, under the charge of Professor Tikholmirov who in recent years has edited eight volumes (1900 pp.) of "Essays on the History of Geological Science." The present text is apparently Part I of a "History of Geology in Russia" largely based on these fuller contributions. The chapters review previous historical writings, the state of geology before 1800, the organization of the mining-geological services, the development of geological mapping, the principal advances in European Russia, the Ukraine, the Urals, the Caucasus, and Asiatic Russia, and the work of Russian geologists in other lands. The plates comprise part of an interesting "petrographical" map covering 18,000 square versts (about 20,000 sq. km) of the Donetz hills in the western Ukraine, dated 1829, and a colored reproduction of the geological map of European Russia and the Urals (in German) by A. K. Meiendorf, dated 1841.

Materialy po geologii rudnykh mestorozhdenii, petrografii, meneralogii i geokhimii. [Contributions on the geology of ore deposits, petrography, mineralogy and geochemistry.] Pp. 424. Academy of Sciences, Moscow, 1959. Price, 25r. 10k.

In an anniversary symposium the younger research workers of the "Institute for the Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry" present 34 short contributions of the kind which, in the West, would be published in ECONOMIC GEOLOGY. The range of these articles is too wide to be summarized briefly but papers on geochemical prospecting for lead, beryllium, molybdenum, lithium and uranium ores merit specific mention.

Osnovy obshchei paleogeografii. [Principles of palaeogeography.] By L. B. RUKHIN. Pp. 557. Gostoptekhizdat, Moscow, 1959. Price, 17r.

The late Professor Rukhin of Leningrad University compiled many important textbooks on sedimentation and the sedimentary rocks, and in this last work he has given us a University manual of quite an unusual kind that displays the great breadth of his knowledge and emphasizes the loss to geological science brought about by his recent death. His lengthy book deals with the principles and methods of palaeogeographical investigations and with the extrapolation of the conclusions drawn from such studies to problems of economic geology. In fourteen chapters one finds a review of the world's literature in this field, drawn in roughly equal proportions from Russian- and English-language sources and illustrated by many sketch-maps and diagrams. There is much information on palaeoclimates, on the meaning of palaeoecology, and on the deciphering of sedimentary structures in terms of contemporary landscape and sea-floor conditions. No single Western text-book known to the reviewer gives a comparable exposition of the detective work of geology, and although it may well be that Rukhin's reconstruction of the former face of the earth is not always the right one, this inexpensive monograph on clues and their interpretation must do much to popularize stratigraphical studies in the U.S.S.R.

C. F. DAVIDSON

UNIVERSITY OF ST. ANDREWS,
SCOTLAND,
September 15, 1960

Geology of the East Tintic Mountains and Ore Deposits of the Tintic Mining Districts. Pp. 183; figs. 33. Utah Geol. Soc. Guidebook Number 12, Salt Lake City, 1959. Price, $4.00

Deep in the heart of Utah, close to its geographical center, is a famous mining district whose recorded production of ore reached the impressive total of $425,000,000. The introduction to the guidebook states "the important metal values are in silver, lead and gold with subordinate values in copper and zinc. Halloysite clay is now an important product of the Main Tintic district, and of much lesser importance is silica rock."

U. S. Highway 50-6 passes through the district, between Provo, Utah, and Ely, Nevada. It is about 60 air miles south of Salt Lake City.

The three Tintic mining districts occupy an area of about 25 square miles in the central part of the East Tintic Mountains, but mining has come to a stop except for recent explorations by Bear Creek Mining Co.

Ore in this area was first discovered in 1869 but the peak of activity was not reached until several decades later. Since 1910, activity gradually declined to

near the vanishing point, until the Bergin shaft was sunk recently and new hidden ore bodies disclosed.

The book being reviewed here will be welcomed by geologists generally but, more particularly, by "hard rock" geologists.

The earliest report on the district seems to have been by Tower and Smith and published in the 19th Annual Report of the U. S. Geological Survey, in 1898 or 1899. S. F. Emmons joined these two geologists in preparing Folio 65 of the U. S. G. S. Geological Atlas, published in 1900. In 1914, G. F. Louglin published an article in ECONOMIC GEOLOGY. These appear to be the only publications prior to World War I.

In 1915, an article by Waldemar Lindgren was published in ECONOMIC GEOLOGY, and the same author, together with G. F. Loughlin and V. C. Heikes, produced U. S. G. S. Professional Paper 107, published in 1919. In 1917, G. W. Crane published an article in the A. I. M. E. Transactions.

Between the two wars, the classic, U. S. G. S. Professional Paper 111 on the "Ore Deposits of Utah," by Butler, Loughlin and Heikes, was published in 1920. There were also publications by Crane (1926 and 1927), Billingsley (1933), Billingsley and Crane (1933), Farmin (1934), Nolan (1935), and an unpublished thesis by Kildale (1938). The most significant article published since World War II is "Economic Geology Monograph 1" by T. S. Lovering et al. in 1949. In the fifties, are articles by Almond and Morris in 1951, Morris and Lovering in 1952, Cook and Berg in 1955, and Kerr in 1955. Papers on the East Tintic area by Lovering and Morris, and by Bush and Cook are in press in ECONOMIC GEOLOGY.

The introduction to the book states: "Two projects have been undertaken in recent years by the U. S. Geological Survey in the East Tintic Mountains. The first project was established in 1942 under the direction of T. S. Lovering and was completed in 1954; it consisted primarily of a study of the geology, hydrothermal wall-rock alteration, and ore reposits of the East Tintic district. The second project, begun in 1954 under the direction of Hal Morris, has not been completed. It consists of a study of the geology of the entire East Tintic Mountains with particular emphasis on the regional setting and possible extensions of the mineralized areas of the Main Tintic and North Tintic districts."

The authors of the papers in the guidebook are taken from the Bear Creek Mining Co., the U. S. Geological Survey, the Chief Consolidated Mining Co., the Anaconda Co., and the International Smelting and Refining Co. Douglas R. Cook, of the Bear Creek Mining Co., is the editor.

The articles cover General Geology (Morris), followed by a series of articles on Ore Deposits: The Main Tintic District (Cook), Chief Mine (Evans), Dragon Mine (Kildale and Thomas), East Tintic Mining District (Bush), Tintic Standard, North Lily and Eureka Lilly Mines (Kildale), Eureka Standard, Apex Standard and Iron King Mines (Bush), North Tintic Mining District (Disbrow and Morris).

There is an article on Hydrothermal Alteration and a Summary of Exploration, both in the East Tintic Mining District, and both by Frank H. Howd. At the back of the book are the road logs. Several of the articles are followed by good bibliographies.

The stratigrapher will find what he is looking for in 27 pages of Morris' article. The rocks range in age from Precambrian to Tertiary, and include representatives of all the systems except those of Mesozoic age. They include about 25 formations, which are illustrated by four columnar sections. The greatest thicknesses are in the Cambrian, Mississippian and Permian systems. The thickest individual forma-

tions are the Lower Cambrian Tintic Quartzite (2,300–3,200 feet), the Upper Mississippian Great Blue Limestone (2,400–2,600 feet), and the Pennsylvania-Permian Oquirrh formation (15,000 feet or more).

Production of ore has come from a wide range of formations, from Lower Cambrian to Upper Eocene. The largest individual producer has been the Bluebell, of Devonian-Silurian age, with a production of $110,000,000. Next comes the Ophir, of Middle and Lower Cambrian age, with a production of $84,500,000, followed by the Ajax of Upper Cambrian age, $60,500,000. The others range down to the Upper Cambrian Cole Canyon, with $7,000,000.

The article by Morris is by far the most comprehensive, comprising one-third of the entire book. Douglas Cook's article on the Main Tintic Mining District consists of 23 pages. The other larger articles are: Ore Deposits of the Tintic Standard, North Lily and Eureka Lilly Mines; Ore Deposits of the North Tintic Mining District; and Ore Deposits of the Chief Mine.

Morris devotes about 11 pages to extrusive and intrusive igneous rocks, and about 14 to structure, of which 9 have to do with faults. The main folds are the North Tintic Anticline, the Tintic Syncline and the East Tintic Anticline. His article ends with a summary of geologic history.

As to the future prospects of the district, Douglas Cook has the following to say: "The ore zones are surprisingly continuous in their strike, persisting for distances of 8,000 to 9,500 feet. Only the Chief ore zone has been intensively mined below the water table, although recently this operation was discontinued. The failure to explore the Chief ore zone down dip and to follow the Gemini ore zone beneath the water table was entirely the result of adverse economic factors rather than exhaustion of ore. We now have reason to believe that the Gemini and Chief ore zones continue to the north, and we believe that the Godiva and Iron Blossom ore zones also continue in a northerly direction."

"Aggressive exploration based on sound geologic principles has shown that important concealed ore bodies are present in the East Tintic district. No geologic reason is evident why new concealed centers of mineralization should not exist in the Main Tintic district. The northern development of some of the ore zones was curtailed because of economic factors; it is conceivable therefore that given more favorable conditions these zones can be followed to greater depths.

"The possibilities of nonmetallic products such as halloysite and silica which have recently been successfully developed should not be overlooked."

"Several large mining companies have engaged in exploration work in recent years in the Tintic mining districts, and currently the Bear Creek Mining Company is drifting from an exploration shaft and doing surface diamond drilling."

According to Max T. Evans, "The Chief mine has produced a large quantity of ore, but it currently is not in operation. Much undeveloped ground remains with many geologically attractive targets. Doubtless the mine will some day be reopened, but its future and the future of the entire district rest solely on economic, not geologic, factors."

On the subject of halloysite, Kildale and Thomas have this to say: "The present limited amount of development work below the 300 level is not sufficient to indicate what the total tonnage of this material may be, but, as developed to date, it is apparently the largest known massive concentration of nearly pure halloysite."

The Utah Geological Society is to be congratulated upon the excellent quality of this publication, the principal responsibility for which seems to have fallen upon Douglas R. Cook and Hal T. Morris.

This much-delayed review would not be complete without quoting the following statements from a recent letter received by the reviewer from Hal Morris: "It is

unfortunate that we undertook to prepare a guidebook on the Tintic area before Bear Creek Mining Co. made its impressive discoveries in the Burgin mine. However, as Bear Creek continues exploration other discoveries may be made that may be the subject of future field trips to the area."

MARTIN VAN COUVERING

PASADENA, CALIF.,
June 7, 1960

Water Witching U.S.A. By E. Z. VOGT and R. HYMAN. Pp. 248. The University of Chicago Press, 1959.

The most complete and scientific answer as to date, to the old question of water witching has been given in this book. It is outstanding both, in contents and in style. It can be recommended very highly to all geologists who agree that an integrated approach to scientific problems is a prerequisite for progress. By integrated we mean in this case an approach that answers geological problems in terms of geology and psychological problems in terms of psychology. And the question of water witching is obviously not only geological. Therefore the answers provided by Vogt and Hyman include a psychological and historical approach.

The appendix on "Water-well Location by Scientific Divination," by H. E. Thomas of the U. S. Geol. Survey is an addition which adds much to the value of the present book. It may be added that this book is dedicated to the County Agricultural Extension Agents. May all of them read it and spread the attitude displayed in it, because it marks a red-letter day in the history of groundwater exploration and in the elimination of superstitions.

G. C. AMSTUTZ

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Journal of Petrology, Vol. I, No. 1. Editors, T. F. W. BARTH, C. E. TILLEY, L. R. WAGER, and H. S. YODER. Clarenden Press, Oxford University. Price, 30/.

Everyone will welcome this new journal to provide an area of publication for original researches in the broadening field of petrology. The cover states that the subjects will include "the physics and chemistry of rocks, their mineralogy and textures, and certain aspects of petrology that involve the dating of rocks by natural radioactivity. Quantitative studies of rock-forming minerals, and parts of isotope geology will appropriately find a place. Regional studies, unless they lead to results fundamental to the science of petrology, will not usually be considered suitable to the journal." This is quite a broad field.

The volumes will consist of three numbers per year—in February, June, and October. The subscription price is 80s. or $12.00.

The first number (March) consists of six articles, as follows: Wyllie, P. J., and Tuttle, O. F., The System, $CaO—CO_2—H_2O$ and the Origin of Carbonatites; Tilley, C. E., Differentiation of Hawaiian Basalts: Some Variants in Lava Suites of Dated Kilauean Eruptions; Hamilton, D. L., and MacKenzie, W. S., Nepheline Solid Solution in the System $NaAlSiO_4—KAlSiO_4—SiO_2$; Wager, L. R., Brown, G. M., and Wadsworth, W. J., Types of Igneous Cumulates; Zies, E. G., and Chayes, F., Pseudoleucite in a Tinguaite from the Bear-paw Mountains, Montana; and Dietrich, R. V., Banded Gneisses.

We wish the new journal all success.

Geology: Principles and Processes, 5th Edit. By W. H. EMMONS, IRA S. ALLISON, CLINTON R. STAUFFER and GEORGE A. THIEL. Pp. 492. McGraw-Hill Book Co., New York, 1960. Price, $7.95.

This greatly revised 5th Edition is completely reset in two-column format, on large pages that permit illustrations 7¾ inches across. The presentation is also different in that minerals, vulcanism, igneous and sedimentary rocks are treated early, as an aid to concurrent laboratory work. Wind and ground water follows, rather than precedes, stream erosion, glaciation, and shore processes. Economic features are treated throughout the text rather than in a separate chapter. A noteworthy feature is that all of the many line drawings are in brown, yellow, gray, and black.

The present order of treatment is as follows: Geology—a Science; Earth as a Planet; Atoms, Radioactivity, and Geologic Time; Land, Sea, and Air; Minerals; Vulcanism; Igneous Rocks and Associated Ores; Rock Weathering and Soils; Sedimentation and Sedimentary Rocks; Gradation by Gravity, and by Running Water; Snow, Ice, and Glaciers; Sea Movements; Ground Water; Wind; Lakes and Swamps; Rock Deformation and Mountain Building; Metamorphism and Metamorphic Rocks; Earthquakes and the Interior of the Earth. There are also four appendices on maps, map symbols and geologic sections; 52 chemical symbols, key to identification of rocks; and an excellent glossary.

The book is nicely written, and the subject matter is interestingly presented. Abundant illustrations add greatly to the text. This new edition should find a wide place as an elementary textbook.

Physical Geography, 2nd Edit. By ARTHUR N. STRAHLER. Pp. 532. John Wiley & Sons, Inc., New York, 1960. Price, $7.50.

This new edition shows many new additions to its popular predecessor. The general outline is similar with four parts—The Earth as a Globe, Weather Elements, Climate and Soil, and Landforms. The chief additions to be noted are the introduction of the Köppen climate system; two new chapters with fundamentals of surface and ground water hydrology; stereographic grid systems; new information on upper air westerlies, jet streams, and tropical easterlies; a new chapter on the Earth's crust including a table on historical geology. Also to be noted are numerous new illustrations including many fine drawings. The new treatment provides a broad natural science base germane to the problems of regional, economic, cultural, and historical geology, and particularly their aids and limitations to the activities of man.

The revised edition should find an important place in the teaching of elementary geography.

Bradley Volume. American Journal of Science, Volume 258-A, 1960.

The American Journal of Science has outdone itself in bringing forth this outstanding and large "Bradley Volume" in honor of Wilmot Hyde Bradley on his sixty-first birthday. Bradley has been with the U. S. Geological Survey since 1921, and for the last fifteen years has been Chief Geologist, until he relinquished this position to pursue his own research.

The volume contains 38 papers by authors drawn from the Survey and American universities and institutions. The subjects covered range widely through paleontology, stratigraphy, sedimentation, geomorphology, structural geology, mineralogy, petrology, and geochemistry. The many authors are all well known in their respective fields.

The volume will be an excellent reference work and should be in everyone's library. It will stand with the other commemorative volumes brought out by the American Journal of Science in its 142 years of existence.

BOOKS RECEIVED

JOHN E. COTTON AND ROGER L. AMES

Classics in Science—A Course of Selected Reading, by AUTHORITIES. Pp. 332. Philosophical Library, Inc., New York, 1960. Price, $6.00. *Selected Classical readings on the Origin and Meaning of Science; the Universe; Matter and Energy; and Science and Everyday Life, drawn from 43 authors, ranging from Aristotle to recent authors. Interesting reading.*

Geology of India and Burma, 4th Edit., by M. S. KRISHNAN. Pp. 604; figs. 14; pl. 22. Higginbothams Ltd. Madras, 1960. Price, Rs. 22.50. *Generally similar to the 3rd edition (1956) but with introductions to each stratigraphical system indicating relationships of Western European units with those of India, also revision of the Jurassic system. The geographic realignment of Indian states has been corrected for the geography of the geology. Black and white maps of the geology of India are included. It is still a textbook for post-graduate students in geology and an advanced treatise on Indian stratigraphy.*

Illustration Guide for Bureau of Mines Publications, by STAFF, Office of Mineral Reports. Pp. 79; figs. 44. U. S. Dept. of Interior Bureau of Mines. *A valuable guidebook on the use of illustrations in technical reports.*

Petroleum Sourcebook 1959. A Regional Bibliography of Petroleum Information. Pp. 234. Price, $7.50. National Petroleum Bibliography (Curtis Stevens, Editor), Amarillo, 1960. *A directory of information sources classified by country, region, state, or province.*

Topographic Instructions. Multiple Plotter Procedures. Pp. 45; figs. 21. U. S. Geological Survey, Dept. of the Interior Book 3, Chapter 3F4, Washington, 1960. *Instructions in the standard operating procedures for the multiplex plotter, including a description of equipment.*

Le Précambrien du Gabon Occidental en Afrique Équatoriale Française et Régions Limitrophes. JEAN-PIERRE DÉVIGNE. Bulletin de la Direction des Mines et de la Géologie, No. 11. Pp. 315; pls. 18; figs. 5; diagrams 5; maps 3—scale 1/500,000. Afrique Équatoriale Haut-Commissariat de la République, 1959. *A doctoral thesis on the structure and petrology of the Precambrian and Cambrian rocks of western Gabon.*

Les gisements de Cassitérite et de Columbo-tantalite du Nord Lugulu, Kivu, Congo Belge. NICOLAS DE KUN. Annales de la Société Géologique de Belgique, Vol. LXXXII, Liège, 1959. Pp. 115; pls. 3; figs. 43. *The North Lugulu placer belt lies between the Kasese batholith and the Karroo transgression of Lugulu Valley. The ore formations were deposited conformably to Precambrian schists.*

Geology of the Kemano-Tahtsa Area. R. A. STUART. Pp. 52; pls. 26; figs. 17. Bull. 42, British Columbia Department of Mines and Petroleum Resources, 1960. *A report on the general geology of the Kemano-Tahtsa area at the eastern border of the Coast intrusions.*

Notice Explicative sur la Feuille Yaoundé-Ouest. G. CHAMPETIER DE RIBES and D. REYRE. Pp. 6–27. Map, scale 1/20,000,000. République du Cameroun,

1959. *The explanatory text of the geologic map of Yaounde West on the Cameroun-Guinea border.*

Proceedings of the Geological Society of China, Number 3 for 1959. Pp. 132. Taipei, Taiwan, 1960. *A series of six articles related to the geology of Taiwan. In English.*

Paleozoic Solenoporaceae and Related Red Algae. J. HARLAN JOHNSON. Pp. 77; pls. 23; tbls. 7; maps 7. Price, $1.25. Quarterly of the Colorado School of Mines Vol. 55, No. 3, Golden, 1960. *The basic algal structures are discussed and the general ideas of classification are given.*

Annual Report of the Geological Survey Department for the Year 1959. F. T. INGHAM, Director. Pp. 5–54. Price, 100 mils. Nicosia, Cyprus, 1960. *A series of areal geology summaries are given.*

Geology of Singatoka Area Viti Levu. R. E. HOUTZ. Pp. 19; fig. 1; photos 2. Map, scale 1/50,000. Price, 12s. 6d. Bull. 6, Geological Survey of Fiji, Suva, 1960. *Four small base metal deposits were found; one may be significant.*

Die Uran- und Goldlagerstätten Witwatersrand—Blind River District—Dominion Reef—Serra de Jacobina: Erzmikroskopische Untersuchungen und Ein Geologischer Verleich. PAUL RAMDOHR. Pp. 35. Abhandlungen der Deutschen Akademia der Wissenschaften zu Berlin, 1958. *A critical comparison of the gold and uranium deposits of the Witwatersrand, Blind River district, Dominion Reef and Serra de Jacobina based on ore microscopy. In German.*

Placer Deposits of the Elk City Region. ROLLAND R. REID. Pp. 25; figs. 8; tbls. 4. Pamphlet 121, Idaho Bureau of Mines and Geology, Moscow, 1960. *Tertiary sands and gravels in the Elk City region appear to contain more thorium, uranium, titanium and zirconium than the stream placers. The heavy minerals were probably derived from the underlying biotite gneiss.*

Oil and Gas in Montana. Revision of 1959. EUGENE S. PERRY. Pp. 86; pls. 2; figs. 23; tbls. 4. Map, scale 1:500,000. Price, $1.50. Montana Bureau of Mines and Geology, Butte, 1960. *This report gives a brief history of oil development in Montana, the general geology and stratigraphy of central and eastern Montana, and the occurrence of oil and gas.*

Suburban and Rural Water Supplies in Southeastern New Hampshire. Pt. XVIII—Mineral Resources Survey. T. R. MEYERS and EDWARD BRADLEY. Pp. 5–31; pl. 1; figs. 7. Map, scale 1 in./1.5 miles. *A layman's guidebook to hydrology and water supply features.*

Changes in Water Levels in 1955 and Annual Water-Level Measurements in January and February 1956 in Observation Wells in New Mexico. H. O. REEDER and others. Pp. 139; figs. 31; tbls. 16. New Mexico State Engineer Technical Rept. 16, Santa Fe, 1960. *Water levels continued to decline in 1955 in most areas where ground water was used for irrigation.*

Annual Report of the Geological Survey Department for the Year Ended 31st December 1959. Pp. 3–19; fig. 1; tbl. 1. Price, 3s. 0d. Printed and published by the Government Printer, Zomba, Nyasaland. *This report is dominantly administrative with only general reference to the major events of the year.*

Oil and Gas Developments in Pennsylvania in 1959. W. S. LYTLE, J. M. BERGSTEN, A. S. CATE, and W. R. WAGNER. Pp. 55; pls. 6; figs. 5; tbls. 11. Pennsylvania Geological Survey Progress Rept. 157, Harrisburg, 1960. *Exploration in 1959 resulted in the discovery of a new gas field and 6 gas pools.*

Report of the Geological Department 1958/1959. Pp. 19. Price, two shillings and sixpence. Sierra Leone Government, Freetown, 1960. Mica Deposits of Northern Sudan. M. L. KABESH. Pp. 55; pls. 11; tbls. 3; charts 7. Republic of the Sudan Geological Survey, Bull. 7, 1960. *Combines the purposes of being an academic paper as well as being a mica miner's pocket book.*

A Guide to the Known Minerals of Turkey. Revised by C. W. RYAN, 1957. Pp. 196. Map, scale 1/2,500,000. Mineral Research and Exploration Institute of Turkey and Office of International Economic Cooperation, Ministry of Foreign Affairs, Ankara, 1960. *A reprint of an edition published in 1957 with only minor changes in text.*

Explanation of the Geology of Sheet 87 (Rakai). W. J. PHILLIPS. Pp. 48; figs. 13; pls. 2; tbls. 2. Map, scale 1/100,000. Price, Shs. 1s/–. Geological Survey of Uganda Rept. 2., Entebbe, 1959. *A petrographic and structural study of the Rakai area west of Lake Victoria.*

Miscellaneous Reports for 1956. Pp. 206; pls. 35 (in separate atlas). Western Australia Geological Survey Bull. 113, Perth, 1958. Also, **Bull. 7, Iron Ores in Western Australia.** R. R. CONNOLLY. Pp. 103. Perth, 1959. *Present exploration has revealed two new iron deposits in Western Australia, Ioolan Island and Cockatoo Island.*

Oil and Gas Report on Lewis and Gilmer Counties, West Virginia. O. L. HAUGHT. Pp. 14; pl. 1; figs. 3. Map, scale 1/62,500. West Virginia Geological Survey Bull. 18, Morgantown, 1960. *An outline of the local geology is given and prospects for future exploration are considered.*

Federal Programs for Collection of Data on Water Use. Pp. 43. Price, 35 cents. U. S. Dept. of Health, Education, and Welfare Notes on Hydrologic Activities; Bull. 10, Washington, D. C., 1960. *An inventory of the present types of water-use data to promote interagency coordination.*

A Primer on Water. L. B. LEOPOLD and W. B. LANGBEIN. Pp. 50; figs. 16. Price, 35 cents. U. S. Geological Survey, Washington, D. C., 1960. *A general review of hydrology and water usage written in nontechnical language for the layman.*

Bureau of Mineral Resources, Geology and Geophysics, Commonwealth of Australia, 1958–1960.

Rept. 38. Papers on Western Australian Stratigraphy and Palaeontology. A. A. OPIK, G. A. THOMAS, P. J. JONES, MARY E. WHITE, and others. Pp. 118.

The Geology of the Eastern Central Highlands of New Guinea. N. J. McMILLAN and E. J. MALONE. Pp. 57; figs. 2; tbls. 2. Map 1, scale 1″/2 mi. *Regional mapping revealed no new economic deposits.*

Rept. 47. Stromatolites from the Paradise Creek Area, North-Western Queensland. W. A. ROBERTSON. Pp. 13; pl. 27; fig. 1. *Stromatolites are morphologically described and found to be of no value in correlating separated regions.*

Bull. 32. The Geology of the Canberra City District. A. A. ÖPIK. Pp. 99; figs. 46; tbls. 5. Maps 2, scale 1″/1 third mi. *A general geologic report.*

Bull. 57. Upper Cretaceous Foraminifera from the Toolonga Calcilutite and the Gingin Chalk, Western Australia. D. J. BELFORD. Pp. 198; pls. 35; figs. 14. *One hundred and thirty-nine species of foraminifera belonging to 56 genera are recorded.*

Vol. 12, No. 4, The Australian Mineral Industry Quarterly Review and Quarterly Statistics. Pp. 104. Price, 3/–. *Contains information up to May, 1960.*

Geological Survey of Canada—Ottawa, 1959–1960.

Bull. 59. The Jurassic Faunas of the Canadian Arctic. Lower Jurassic and Lowermost Middle Jurassic Ammonites. HANS FREBOLD. Pp. 33; pls. 15; figs. 8; tbl. 1. Price, $1.25. *Most of the ammonites belong or are related to species of world-wide distribution.*

Bull. 60. Canadian Fossil Arthropoda Eurypterida, Phyllocarida and Decapoda. M. J. COPELAND and T. E. BOLTON. Pp. 84; pls. 11; figs. 10; tbls. 5. Price, $1.25. *Discussion of 24 species which were found; many are new species or previously unrecorded in Canada.*

Memoir 303. Surficial Geology of Sturgeon Lake Map-Area, Alberta. E. P. HENDERSON. Pp. 108; pls. 13; figs. 8. Map, scale 1/253,440. Price, $1.00. *Three tills are recognized in the region.*

Memoir 307. Atlin Map-Area British Columbia. J. D. AITKEN. Pp. 89; pls. 4; figs. 11; tbls. 3. Map, scale 1/253,440. Price, $1.00. *More than $16 million worth of placer gold have been mined in the region.*

Memoir 314. Mississippian Horton Group of Type Windsor-Horton District, Nova Scotia. W. A. BELL. Pp. 112; pls. 24. Price, $2.00. *A discussion of the stratigraphy and structure of the non-marine Horton group, and descriptions of plants and invertebrates found in this group.*

Paper 60-2. Triassic Stratigraphy, Rocky Mountain Foothills, Northeastern British Columbia. B. R. PELLETIER. Pp. 32; fig. 1. Price, 50 cents. *A preliminary report on the stratigraphy in the lower and middle Triassic rocks. Contains measured sections.*

Paper 60-6. Geological Interpretation of Aeromagnetic Profiles from the Canadian Arctic Archipelago. A. F. GREGORY, MARGARET E. BOWER, and L. W. MORLEY. Pp. 13; figs. 5. Price, 50 cents. *Magnetic anomalies of geologic significance result in increased interest in the Archipelago.*

Paper 60-7. Summary Account of Structural History of the Canadian Arctic Archipelago Since Precambrian Time. R. THORSTEINSSON and E. T. TOZER. Pp. 25; figs. 4. Price, 50 cents. *The authors divide the region into seven structural provinces.*

Aeromagnetic Maps, scale 1/63,360. Nos. 230G, 240G, 1010G–1014G, 1025G–1026G, Inverness, Victoria and Antigonish Counties, Nova Scotia; Maps 930G–939G, Thunder Bay and Kenora districts, Ontario; Map 1097A, Geology, Rolling Dam, New Brunswick.

Aeromagnetic Maps, scale 1/63,360. Nos. 838G–849G, Gulf of St. Lawrence, Merigomish, Malignant, Boughton Souris, and Port Hood in Nova Scotia and Prince Edward Island; Maps 850G–859G, Wegg, Gullrock, Red, Nungesser and Coli, Kirkness, Berens, McInnes, Critchell, Kennedy, and Favourable Lakes, Kenora District, Ontario; Geology maps, 1082A, Atlin, British Columbia, scale 1/253/440, **1096A, St. Stephen, New Brunswick,** scale 1/63,360; **Map 18-1960 (2 sheets), Mackenzie, N. W. Territories,** scale 1/506,880; **Fernie, B. C., Map 11-1960, geology,** scale 1/126,720.

California Division of Mines—San Francisco, 1960.

Fifty-Sixth Report of the State Mineralogist. IAN CAMPBELL. Pp. 219; figs. 5; photos 16; tbls. 9.

Special Rept. 62. Geology of the Orchard Peak Area. OWEN T. MARSH. Pp. 42; pls. 2; figs. 14; photos 11. Price, $1.00. *The impermeable sole of the Antelope Valley thrust may have trapped petroleum in the underlying Miocene beds.*

Illinois Geological Survey—Urbana, 1960.

Circ. 297. Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks. Pt. 1. Carbonate Mineralogy; Carbonate Sediments. DONALD L. GRAF. Pp. 39; fig. 1; tbls. 3. *Review of carbonate mineralogy and sedimentary environments.*

Circ. 298. Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks. Pt. II. Sedimentary Carbonate Rocks. DONALD L. GRAF. Pp. 43; figs. 6; tbls. 4. *Review of sedimentary environments and their relation to chemical composition of sediment.*

Circ. 299. Sand and Gravel Resources of Kane County, Illinois. D. A. BLOCK. Pp. 11; pl. 1; fig. 1; tbls. 5. *Deposits are classified on a map according to their character and mode of occurrence.*

Circ. 300. Mineral Production in Illinois in 1959. W. L. BUSCH. Pp. 36; figs. 8; tbls. 24. *Total value of mineral production in 1959 was lower than in 1958 by about 1%.*

Consiglio Nazionale delle Ricerche—Rome, 1959–1960.

Analisi e Preparazione dei Minerali. Pp. 9–79. *A collection of abstracts on mineral preparation and analysis. In Italian.*

Il Congresso Internazionale per la Preparazione dei Minerali, Londra 1960. Pp. 107. *The report of a series of symposia on mineral dressing. In Italian.*

Centro di Studi per la Preparazione dei Minerali. Attività svolta nel biennio 1958–59. Pp. 15. (Estratto da La Ricerca Scientifica, Anno 30, No. 6, Giugno 1960.) *Report describes the results of studies covering methods for quick quantitative analysis of metal contents of mercury and uranium ores, separation process of uranium from interfering elements by ion-exchange resins and studies of ore concentration. In Italian; English summary.*

Geological Survey of Japan—Hisamoto-chō, Kawasaki-shi, 1960.

Rept. 184. On the Propagation of Transient Elastic Waves. SHOZABURO NAGUMO. Pp. 50. *The propagation of transient elastic waves in two dimensions is investigated by the method of dual integral transformation. In English.*

Rept. 185. On the Toyosato Barrier and Ashibetsu Basin in the Geo-History of the Deposition of the Upper Ishikari Group, Hokkaido. HIROSHI MATSUI. Pp. 22. Map, scale 1/75,000. *Report on the influence of Toyosato barrier on the Lower Cenozoic sedimentation. In Japanese; English Abstract.*

Kansas Geological Survey—Lawrence, 1960.

Bull. 146. Ground-Water Levels In Observation Wells In Kansas, 1959. V. C. FISHEL and MARGARET E. BROEKER. Pp. 5–174; figs. 25; tbls. 4. *Includes the measurements of water levels in 835 wells in Kansas and shows that there was a small lowering of the water table in most wells during 1959.*

Bull. 147. Oil and Gas Developments in Kansas During 1959. E. D. GOEBEL, P. L. HILPMAN, D. L. BEENE, and R. J. NOEVER. Pp. 254; pls. 3; figs. 12; tbls. 32. *Proved reserves of Kansas crude oil were over 900 million barrels at the end of 1959.*

Bull. 142, Pt. 2. Kansas Building Stone. H. E. RISSER. Pp. 53–122; pls. 13; figs. 5. *Production of cut and finished stone is growing in relation to production of rough building stone.*

Bull. 142, Pt. 3. Lime Raw Materials in the Kansas City Area. WILLIAM IVES and R. T. RUNNELS. Pp. 123–148; pl. 1; figs. 2; tbls. 18. *Three areas of high-purity limestones within 30 miles of industrial districts of Kansas City have been found.*

Data On Secondary Recovery Projects in Kansas, 1959. E. D. GOEBEL, P. L. HILPMAN, D. L. BEENE, and R. J. NOEVER. *Two tables (Sheets No. 1 and 3 of Oil and Gas Investigations No. 20) showing data on Allen through Greenwood and Greenwood through Woodson Counties.*

New Zealand Geological Survey—Wellington, 1959–1960.

Bull. n.s. 40. The Geology of Tongariro Subdivision. D. R. GREGG. Pp. 151; figs. 69; tbls. 31. Maps, 1/63,360. Price, paper cover, £2. *A general geologic report of the Tongariro area is presented and separate appendices given for fossils, petrology of volcanics, and physical and chemical study of Ketetahi Hot Springs.*

Bull. n.s. 66. The Geological Map of New Zealand 1/2,000,000. G. W. GRINDLEY, H. J. HARRINGTON, and B. L. WOOD. Pp. 111; figs. 31; pls. 5. Price, paper cover, £1 7s. 6d. *A revision of the 1947 geological map of New Zealand is available showing many new igneous and metamorphic units and a closer subdivision of the pre-Mesozoic sediments.*

Bull. n.s. 68. Origin of Ignimbrites of the North Island, New Zealand: A New Petrogenetic Concept. A. STEINER. Pp. 7–41; figs. 18; tbls. 5. Price, paper cover, 9s. *The groundmass of ignimbrites is composed of two contrasting glasses, a glassy base and a mesostasis. Liquid immisibility during extrusion is composed of two contrasting glasses, a glassy base and a mesostasis. Liquid immisibility during extrusion is adduced to explain this fact.*

Bull. 136. The Hot Springs and Geothermal Resources of Fiji. J. HEALY. Pp. 76; figs. 12; tbls. 4. Price, 6s. 6d. *The temperature of most of the springs is below 60°C with only two springs boiling. Only the two boiling springs are regarded as economically important.*

Geological Map of New Zealand Sheet 27—Fiord. Scale, 1/250,000.

Northern Rhodesia Geological Survey—Lusaka, 1960.

Rept. 6. The Karroo System of the Western End of the Luano Valley. H. S. GAIR. Pp. 40; pls. 3; map 1. Price, 15s. *The coal measures of the Karroo sequence in this area are thin seams of high-ash coal and are not economic deposits.*
Annual Report for the Year 1959. Pp. 10. Price, 2s.

Ontario Department of Mines—Toronto, 1960.

Volume LXVIII, Part 1, 1959. Statistical Review of the Mineral Industry for 1958. T. J. KELLY. Provincial Assay Office, 1958. D. A. MODDLE.

Mining Accidents in 1958. STAFF OF MINES INSPECTION BRANCH.

Classes for Prospectors, 1958–59. W. D. HARDING. Pp. 46.

Bull. 25. List of Publications (Revised to April, 1960). Pp. 71. Price, 25 cents.

Union of South Africa Department of Mines—Pretoria, 1959–1960.

Memoir 48. The Geology of the Richtersveld. JOHN DE VILLIERS and P. G. SÖHNGE. Pp. 266; pls. 38; figs. 16. Folders 4. Price, £1. 15s. 6d. *Geologic*

mapping of nearly 3,000 square miles in northwestern Namaqualand has revealed few economic deposits. Diamonds are presently mined from beach gravels on uplifted terraces.

Information Pamphlet 6. Pegmatites: Hints to Prospectors. B. Booyseh. Pp. 57. *An elementary summary of pegmatite geology, mining techniques, and characteristic pegmatite minerals.*

Bull. 30. Die Steenkoolveld Standerton State Van Boorgate 1 Tot 13. K. H. L. Sehlke en S. W. van der Merwe. With a summary in English entitled: **The Standerton Coal-field Records of Bore-Holes 1 to 13.** Pp. 63; tbls. 5. Map, scale 1/50,000. Price, 5s. 6d. *Part 1 covers the geology of the Standerton coal-field, and Part 2 is a report of the chemical and physical properties of the coal.*

Bull. 31. The Northeastern Springbok Flats Coal-Field. Records of Bore-Holes 1 to 27 Drilled for the Department of Mines. With notes by H. N. Visser and S. W. van der Merwe. Pp. 97/ Map, scale 1/150,000. Price, 9s. 3d. *Only two small portions of the region are likely to be potential coal fields.*

Bibliography and Subject Index of South African Geology 1958. Pp. 49. Price, 2s. 6d.

Maps (2): Volksrust map, colored, scale 1/250,000. **Volksrust Coal Field map,** scale 1/75,000.

Virginia Division of Mineral Resources—Charlottesville, 1960.

List of Publications and Maps. Pp. 3–27. Price, $1.00.

Rept. of Investigations 1. Geology of the Lexington Quadrangle Virginia. K. F. Bick. Pp. 40, pl. 1; tbl. 1. Map, scale 1/62,500. *The general geology of the area is presented, and economic considerations show limestone to be the only potential resource.*

Information Circ. 2. Water-Well Data Western Part of Albemarle County. Whitman Cross II. Pp. 16. Map, scale 1″/1.7 miles. *A compilation of approximately 300 drilled wells is given.*

U. S. Geological Survey—Washington, D. C., 1960.

Bull. 1045-F. Core Logs from Five Test Holes Near Kramer California. W. C. Benda, R. C. Erd, and W. C. Smith. Pp. 319–393; pls. 2; fig. 1; tbls. 3. *In two test holes an unusual ferromagnetic iron sulfide is abundant. It is fine-grained, soft, and grayish black; it gives a unique x-ray powder pattern.*

Bull. 1072-H. Geology and Thorium Deposits of the Wet Mountains, Colorado—A Progress Report. R. A. Christman, M. R. Brock, R. C. Pearson, and Q. D. Singewald. Pp. 491–535; pls. 2; figs. 3; tbls. 7. *More than 800 radioactivity anomalies (due almost entirely to thorium) were found in this area of Precambrian rocks.*

Bull. 1082-D. Beryl-bearing Pegmatites in the Ruby Mountains and Other Areas in Nevada and Northwestern Arizona. J. C. Olson and E. N. Hinrichs. Pp. 1–200; pl. 37; figs. 8–11; tbls. 1–7. Map, scale 1″/500 ft. *Reconnaissance for beryl-bearing pegmatites in Elko County, Nevada and Mohave County, Arizona has shown 11 districts.*

Bull. 1082-E. Strategic Graphite—A Survey. E. N. Cameron and P. L. Weis. Pp. 201–321; pls. 8–11; figs. 12–32; tbls. 2. Price, $1.25. *A comprehensive survey of the uses, production, and geology of the graphite districts in Montana, Texas, Alabama, Pennsylvania, and New York.*

Bull. 1083-D. Pulse-Transient Behavior of Brine-Saturated Sandstones. G. V. KELLER. Pp. 111–129; figs.; 36–44; tbls. 1–4. Price, 15 cents. *Describes electrical polarization in sandstone and possible explanations of the source.*

Bull. 1084-F. Spectrophotometric Determination of Traces of Lead in Igneous Rocks. C. E. THOMPSON and H. M. NAKAGAWA. Pp. 1–164; figs. 22–27; tbls. 1–4. *A quantitative method for the determination of traces of lead in rocks high in iron and zinc.*

Bull. 1084-G. Method for the Quantitative Spectrochemical Analysis of Rocks, Minerals, Ores, and Other Materials by a Powder D-C Arc Technique. HARRY BASTRON, P. R. BARNETT, and K. J. MURATA. Pp. 165; tbls. 1–3. Price, 15 cents. *The D-C arc source of excitation provides good detectability of low concentration elements because a relatively large amount of sample is consumed.*

Bull. 1085-A. The Development of Botanical Methods of Prospecting for Uranium on the Colorado Plateau. HELEN L. CANNON. Pp. 1–50; pls. 1–5; fig. 1; maps 2, scale 1″/30 mi. *A fluorimetric method and a chromatographic test have been devised to detect anomalously large amounts of trace elements in herbaceous plants.*

Bull. 1085-B. Botanical Prospecting for Uranium in the Deer Flat Area White Canyon District, San Juan County, Utah. A. J. FROELICH and F. J. KLEINHAMPL. Pp. 51–84; pls. 6; figs. 2; tbls. 2; map scale 1″/1,000 ft. Price, 65 cents. *Botanical anomalies occur at all known ore bodies in the Deer Flat area which suggests that other anomalies may be associated with mineralized ground. Recommendations for exploration are given.*

Bull. 1085-C. Botanical Prospecting for Uranium in the Circle Cliffs Area, Garfield County, Utah. F. J. KLEINHAMPL and CARL KOTEFF. Pp. 85–104; pls. 2; fig. 1; tbls. 3. *The plant-analysis method in this area may be used to locate uranium in the Shinarump member even when the deposits lie as much as 70 feet below the surface.*

Bull. 1071-G. Geomorphology of the Upper Kuskokwim Region, Alaska. A. T. FERNALD. Pp. 191–279; pls. 2; figs. 8–37. *A reconnaissance study of the Upper Kuskokwim region in southwest-central Alaska covering physiographic features, glacial history, and surficial deposits.*

Prof. Paper 260-X. Smaller Foraminifera from Eniwetok Drill Holes, Bikini and Nearby Atolls, Marshall Islands. Ruth Todd and Doris Low. Pp. 799–861; pls. 10; figs. 4; tbls. 7.

Prof. Paper 260-Y. Drilling Operations on Eniwetok Atoll, Bikini and Nearby Atolls, Marshall Islands. H. S. LADD and S. O. SCHLANGER. Pp. 863–903; pls. 2; figs. 28; tbls. 3. *Leached zones (indicated removal of aragonite of its recrystallization to calcite) are thought to record periods when the top of the atoll was above sea level.*

Prof. Paper 282-D. Flow Resistance in Sinuous or Irregular Channels. L. B. LEOPOLD, R. A. BAGNOLD, M. G. WOLMAN, and L. M. BRUSH, JR. Pp. 111–134; pls. 2; figs. 13; tbls. 5. Price, 25 cents. *There may be a marked increase in resistance to fully developed turbulent flow with excessive deformations of the free surface of the stream due in turn to deflections of the flow by irregular flow boundaries, i.e., channels.*

Prof. Paper 282-E. Some Aspects of the Shape of River Meanders. R. A. BAGNOLD. Pp. 135–144; figs. 7. Price, 20 cents. *Resistance to flow in curved channels is least when the ratio, mean radius of curve to diameter of pipe (or width of river), is between 2 and 3.*

Prof. Paper 315-C. Stratigraphic Distribution of Some Pennsylvanian Fusulinidae from Brown and Coleman Counties, Texas. D. A. MYERS. Pp. 37–51; pls. 10; figs. 2; tbl. 1. Price, 45 cents.

Prof. Paper 316-D. Gravity Survey of the Western Mojave Desert, California. D. R. MABEY. Pp. 51–73; pls. 3; figs. 10. *Gravity data will be helpful in developing ground-water resources and exploration for saline deposits and petroleum.*

Prof. Paper 325. Geology of the Souris River Area North Dakota. R. W. LEMKE. Pp. 138; pls. 16; figs. 17. *The Souris River area is entirely mantled with Pleistocene deposits, hence this report is largely Pleistocene geology.*

Prof. Paper 333. The Foraminiferal Genus *Orbitolina* in North America. R. O. DOUGLAS. Pp. 52; pls. 17; figs. 32; tbls. 9. Price, $1.50. *A study of the genus Orbitolina, its type, species, morphology, and stratigraphic and geographic distribution in North America.*

Water-Supply Paper 1454. Methods for Collection and Analysis of Water Samples. F. H. RAINWATER and L. L. THATCHER. Pp. 301; figs. 17; tbls. 3. Price, $1.50. *Topics discussed are selection of sampling sites, frequency of sampling, field equipment, preservatives and fixatives, analytical techniques of water analyses, and instruments.*

Water-Supply Paper 1459-C. Some Chemical Relationships Among Sulfur Species and Dissolved Ferrous Iron. J. D. HEM. Pp. 16; figs. 3. *A discussion of ferrous iron activity in the presence of several species of sulfur, under a variety of Eh-pH conditions.*

Water-Supply Paper 1459-D. Complexes of Ferrous Iron With Tannic Acid. J. O. HEM. Pp. 75–94; figs. 9–10; tbls. 1–3. *Tannic acid is used as a complexing agent in research on the chemistry of iron in natural water.*

Water-Supply Paper 1459-F. A Survey of Pertinent Biochemical Literature. E. T. OBORN. Pp. 111–190; figs. 12–17; tbls. 1–3. *Review of the biochemical factors in the iron cycle.*

Water-Supply Paper 1475-B. Hydrology of Cornfield Wash, Sandoval County, New Mexico, 1951–55. F. W. KENNON and H. V. PETERSON. Pp. 45–103; pls. 5; figs. 12; tbls. 12. Price, 55 cents.

Water-Supply Paper 1487. Geology and Ground-Water Resources of the Lower Little Bighorn River Valley, Big Horn County, Montana. E. A. MOULDER, M. F. KLUG, D. A. MORRIS, and F. A. SWENSON, With a section on **Chemical Quality of the Water** by R. A. KRIEGER. Pp. 223; pls. 13; figs. 37; tbls. 28. *Wells in river alluvium and terrace deposits yield as much as 100 gallons per minute.*

Water-Supply Paper 1488. The Geology and Ground-Water Resources of Calcasieu Parish, Louisiana. A. H. HARDER. Pp. 102; pls. 9; figs. 29; tbl. 9. *The principal water-bearing horizons are in the Chicot aquifer of Pleistocene age.*

Water-Supply Paper 1489. Geology and Ground Water in the Platte-Republican Rivers Watershed and the Little Blue River Basin Above Angus, Nebraska. C. R. JOHNSON. With a section on **Chemical Quality of the Ground Water** by ROBERT BRENNAN. Pp. 142; pls. 4; figs. 11; tbls. 5. *Present ground water supplies are tapped from the Pliocenеic Ogalalla formation and Pleistocene deposits.*

Economic Geology
Vol. 55, 1960, pp. 1776–1778

SCIENTIFIC NOTES AND NEWS

GEORGE A. KIERSCH has joined the faculty of Cornell University to replace Professor C. M. NEVIN, retired. For the past five years Dr. Kiersch has been directing a special large-scale geological mapping and mineral resources survey for the Southern Pacific Co., San Francisco and prior to that was on the faculty of the University of Arizona.

We call attention of all authors and prospective authors to a little booklet published by the U. S. Bureau of Mines, Washington, D. C., entitled "Illustration Guide for Bureau of Mines Publications." This guide will help you prepare illustrations in a suitable manner for submission with manuscripts.

The Missouri School of Mines recently announced the appointment of HUGHES M. ZENOR as professor of geophysics, and ARTHUR H. BROWNLOW as assistant professor in geochemistry in the Geology Department.

J. CAMPBELL CRADDOCK, Assistant Professor of Geology at the University of Minnesota, is spending three months in Antarctica this winter on a research project financed by the National Science Foundation. Five students and a physician are accompanying the party which will return March 1. Mr. Craddock's courses in structural geology at the University of Minnesota are being taught by Dr. E. K. Walton, visiting Assistant Professor at the University of Edinburgh, Scotland.

W. T. HOLSER has been promoted from research geologist to Senior Research Mineralogist in the Geology Research Section, La Habra Laboratory of the California Research Corporation.

VINCENT N. BURNHART has been elected President of the E. J. Longyear Company, Minneapolis, succeeding Donald M. Davidson who died recently.

"The Geological Map of the U.S.S.R.," published four years ago, has been revised under the editorship of D. V. MALIVKIN, particularly for new areas of oil, gas, coal, and iron ore. The largest gas field in the country was found in Bukhara at Gazli, which contains 400,000 million cubic meters of gas. Other recent gas and oil fields are in Kara-Kum desert, and in Turkmenia, Tajikistan, and Kazakhstan. New coal deposits have been found in South Siberia and North Kazakhstan.

JOE WEBB PEOPLES became the new Director of the Connecticut Geological and Natural History Survey on June 1 succeeding JOHN B. LUCKE who resigned from the post. Dr. Peoples is chairman of the Geology Department at Wesleyan University. The office of the Connecticut Geological and Natural History Survey is now Judd Hall, Wesleyan University, and the mailing address is Box 128, Wesleyan Station, Middletown, Connecticut.

HUBERT E. RISSER has been appointed principal mineral economist of the Illinois State Geological Survey, replacing WALTER H. VOSKUIL who has retired. He has been serving as mineral economist since 1957.

ELIS DAHLSTROM has accepted an assignment with the UN's Special Fund as project manager for a mineral survey of parts of northern Chile.

JOAN J. REED has joined the faculty of the Colorado School of Mines as a professor of mining engineering.

THOR H. KIILSGAARD, geologist with the U.S.G.S., recently returned from a three-month trip to Bolivia, where he was a geologic consultant to the U. S. International Cooperation Administration and the Bolivian Government.

R. M. MCALEXANDER, formerly with Gunnison Mining Co., has been appointed mining engineer-geologist with Peru Mining Co. at Hanover, New Mexico.

A. C. M. LAING, formerly geologist with Mines Administration Pty., Ltd., in Brisbane, Australia, has become affiliated with B. P. Shell Todd Development, Ltd., in Gisborne, New Zealand.

ROBERT D. HUTCHINSON has been named Northwest District Geologist for Bear Creek Mining Co., succeeding S. E. JEROME, who resigned in July. Hutchinson has served on the staffs of the Geological Survey of Canada and Union Carbide Ore Co., and has been District Geologist for Kennco Explorations (Canada) Ltd., in central Canada.

A. F. FREDERICKSON has joined the University of Pittsburgh as Chairman of the Department of Geology where an expanded research and graduate training program is being organized. Dr. Frederickson was formerly Professor of Geology at Washington University in St. Louis before he joined the Pan American Petroleum Corporation to organize their geological research program which he supervised for five years prior to joining the staff at Pitt.

RICHARD M. FOOSE, Chairman of the Department of Earth Sciences at Stanford Research Institute, Menlo Park, California, recently returned from an extended visit to Europe and Asia involving geological investigations in Iran, participation at the International Geological Congress meetings in Copenhagen, and a month-long tour of Universities and scientific Institutes in the Soviet Union.

The International Minerals & Chemical Corporation (Canada), Ltd., has been shaft sinking at its potash mine near Esterhazy, Saskatchewan, and is now well into the water-bearing Blairmore sands and proceeding satisfactorily. The shaft is more than halfway through the 200-feet Blairmore, frozen at about — 50° Fahrenheit after a year of freezing. A cast-iron lining through the frozen area is being installed in five-foot rings simultaneous with the sinking.

According to an announcement in the U.S.S.R. by the Publishing House for Foreign Literature (Inostranizdat, Moscow), works to be published during 1961 will include Russian translations of PAUL RAMDOHR's most recent textbook on ore minerals, and E. W. HEINRICH's text on the mineralogy and geology of radioactive raw materials.

BERT S. BUTLER, former professor and head of The University of Arizona's department of Geology and Mineralogy in the College of Mines, and for a long time Associate Editor of this Journal, died in Tucson November 13 in his 83rd year.

RICHARD V. COLLIGAN has been elected vice-president of Freeport Sulphur Co. His last post, which he retains, is that of president of the Moa Bay Mining Co., a Freeport subsidiary.

RONALD R. MCNAUGHTON was elected president of AIME for 1961 succeeding Dr. JOSEPH L. GILSON.

This Journal goes to 102 different countries. The largest number of subscriptions, outside of the United States and Canada, are from Japan, Russia, England and Germany.

JOHN RODGERS has returned to the Department of Geology at Yale University after a year's leave of absence in Europe.

LINCOLN WASHBURN has joined the Department of Geology at Yale University.

PAUL BAILEY has been made President of the Bear Creek Exploration Co., an exploration subsidiary of Kennecott Copper Corp.

S. DOLBEAR of Behre Dolbear Co. has returned from an extended trip to Australia.

CHARLES BEHRE has returned to Columbia University after spending several months in Europe.

P. K. HALL has returned from London to the Geological Survey Department at Sierra Leone.

H. P. T. HYDE has been appointed Professor of Geology at the Humboldt University, East Berlin.

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